Inverted and multiple nematic emulsions

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We investigate experimentally the structures that form when small colloidal particles are suspended in a nematic solvent. These structures are anisotropic, and their formation is driven by interactions arising from the orientational elasticity of the nematic solvent. By using inverted and multiple nematic emulsions composed of water droplets dispersed in a thermotropic liquid crystal, we identify the nature of these interactions, and demonstrate that they can be controlled by the anchoring of the liquid crystal molecules at the surfaces of the droplets. When the anchoring is normal, the droplets form linear chains, suggesting a long-range dipole-dipole attraction between the particles. By contrast, the interactions are repulsive at short range, and prevent contact of the droplets, thereby stabilizing them against coalescence. When the anchoring is planar, the droplets generate distortions that have a quadrupolar character. The resultant elastic interactions lead to more compact, but still anisotropic, clusters. [S1063-651X(98)07701-0]

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I. INTRODUCTION

The distinctive features of nematic liquid crystals arise from the orientational ordering that the liquid crystal molecules adopt [1]. Due to their orientational order, these materials exhibit specific optical properties and responses to external fields which lead to many important technological applications of liquid crystals [1–4]. However, such order makes it difficult to suspend small colloidal particles in liquid crystal hosts, because of the strong elastic distortions which ensue [5]. Nevertheless, if small particles are suspended in liquid crystals, new composite materials result, and the behavior of these particles reflects the ordering of the liquid crystal. Moreover, anisotropic interactions between the particles occur as a result of the elastic distortions of the liquid crystal host [6]. These lead to new colloidal structures, which are of interest as examples of topologically controlled structures; they are also of potential practical importance as a novel way to control both the stability and the structures of colloidal particles.

In this paper, we examine the structures of colloidal particles suspended in a nematic thermotropic liquid crystal. The molecules of a nematic fluid are called nematogens. For the thermotropic liquid crystals used here, the nematogens are long, rigid, rodlike molecules, which pack with a preferred direction, resulting in long-range orientational order [7,8]. The preferred direction of alignment of the molecules is specified by the unit vector field **n**, called the director. When the wavelength of the distortions of **n** is large compared to the size of the nematogens, the distortions can be described in terms of continuum elastic theory. This is the relevant limit for the present study, as the size of the particles is of order a micron, and is thus much greater than the size of the nematogens, which is about 30 Å.

The other energy in these systems comes from the local interactions between the nematogens and the particle surfaces and at the boundaries of the sample; this is the anchoring energy [9]. When the anchoring to a surface is strong, the director makes a well-defined angle with this surface, regardless of the resultant elastic distortions. In this limit the boundary conditions of **n** are fixed. This situation is of great practical interest, as it is commonly encountered in applications of liquid crystal materials. By contrast, in the limit of weak anchoring, the competition between anchoring energy and elastic distortions may lead to different orientations of the director at the interface, and to more complex behavior [10]. If the anchoring energy tends to zero, the director can adopt any orientation at the interfaces and, as required by minimization of the elastic energy [7,8], no elastic distortions are needed. This limit is, however, rarely achieved.

The combination of the geometry and the boundary conditions impose topological constraints which must be satisfied by the director field of the liquid crystal; this can lead to the formation of topological defects [11] which cannot be removed. These topological defects play a crucial role in determining the elastic interactions between colloidal particles suspended in a liquid crystal host.

To identify the nature of these topological defects and the elastic interactions between the particles, we use emulsions, made of water droplets suspended in a continuous liquid crystal phase, or multiple emulsions made of water droplets suspended in much larger drops of liquid crystal which are in turn suspended in water. We investigate two limits of strong anchoring on the surface of the particles: normal, or homeotropic, anchoring, and planar, or tangential, anchoring. These anchoring conditions allow us to study two important limits for the boundary conditions of **n** on the droplets. For normal anchoring the director is normal to the surface of the droplets; for planar anchoring the director is parallel to the surface of the droplets. The control of the anchoring is achieved experimentally by using various amphiphilic compounds which are adsorbed at the water–liquid-crystal interface. Molecular surfactants are used to induce strong normal anchoring, while a polymer is used to induce strong planar anchoring.

The energy scale of an elastic distortion around a particle

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is of order Ka, where K is a typical elastic constant [7,8] of the nematic liquid crystal, and a is the radius of the particle. For a thermotropic liquid crystal K is approximately 10^{-11} N and for a colloidal particle a is approximately one micrometer; thus the energy scale is a few thousands $k_B T$, where k_B is the Boltzmann constant and T the temperature. As a result, the entropic free energy of the particles is negligible compared to elastic interactions; this actually simplifies the experimental investigation, since any structures formed due to attractive interactions remain stable against thermal fluctuations. Control of the strong anchoring and high elastic energy are key advantages of using these nematic emulsions to study the nature of colloidal interactions in nematic solvent. The limits investigated in this work are expected to be useful to build further our understanding of more complex phenomena involving weaker interactions arising from weaker anchoring or elastic constants and smaller size of particles. For example, the singular behavior of latex particles embedded in nematic micellar solutions is clearly a manifestation of elastic phenomena [5,12]. However, the weakness of the elastic constants of such lyotropic systems and the very small size of the particles lead to a complex phase behavior, which makes it more difficult to directly extract information concerning the elastic interactions.

We observe the structure of the systems with optical microscopy. By using crossed polarizers, we identify the nature of the topological defects and map the distortions of **n**. Isolated particles can be observed shortly after the sample preparation. They are always accompanied by defects which allow the topological constraints to be satisfied. For both normal and planar anchoring these companion defects are point defects, although they are different for either case. As time elapses, the particles stick to each other and form anisotropic clusters. The formation of these structures demonstrate the presence of attractive forces; the stability of the particles against coalescence demonstrates the presence of repulsive forces. For normal anchoring the attractive force has a dipolar character, and can be understood using an analogy to electrostatics. This dipolar force leads to the formation of chainlike structures, similar to those seen in other dipolar fluids, such as electrorheological or magnetorheological fluids [13]. At shorter range, an elastic repulsion imposes an equilibrium separation of a few tenths of a micrometer between the particles. The range of this repulsive interaction scales with the particle size. The repulsion arises from the presence of a topological defect between neighboring particles; it prevents two droplets from contacting, and thereby provides a new form of colloidal stabilization. By contrast, for planar anchoring, the droplets assemble in three-dimensional structures where the particles are in contact and where the line joining their center makes an angle of 30° with the axis of alignment of the nematic. This behavior again reflects the existence of anisotropic interactions between the particles. For planar anchoring, the long-range interaction is theoretically expected to have a quadrupolar character. However, although, the equilibrium structures are reminiscent of those expected from quadrupolar interactions, their formation is more likely dominated by short-range interactions.

In Sec. II, we present the essential concepts describing colloidal particles in a nematic liquid crystal, and we briefly review theoretical predictions for the long-range interactions between the particles. Section III describes the preparation of the samples, and explains how the boundary conditions are controlled. The nature of the topological defects accompanying isolated particles is presented in Sec. IV. Section V deals with the experimental behavior of a collection of droplets and the interactions between them. A brief conclusion closes the paper.

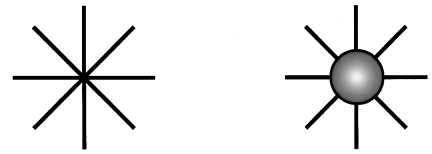

FIG. 1. Schematics of the director field of a radial hedgehog (left), and of a particle with normal boundary conditions (right). The particle and the hedgehog give rise to similar radial configurations, and are topologically equivalent.

II. THEORETICAL MODELS

The first step in understanding the behavior of colloidal particles in nematic fluids consists in determining the structure of the director field around one isolated particle. Here we describe the possible behavior with homeotropic and planar anchoring.

A particle with homeotropic anchoring is in fact equivalent to a topological defect called a radial hedgehog [14]; an example of this is shown in Fig. 1. In the figure, the lines represent the direction of the director, **n**; with radial symmetry in the far field, the director lines must meet at a central point, resulting in the topological defect. Hedgehogs are point defects in which the director sweeps out all directions on a unit sphere an integral number of times on a spherical surface enclosing the defect. These defects can be characterized by a topological charge [14]; this is the integer specifying the number of times the unit sphere is wrapped by the director. In liquid crystals, **n** is equivalent to $-\mathbf{n}$ and, as a result, hedgehogs with positive and negative charges are indistinguishable. Thus hedgehogs in liquid crystals are characterized by positive charge only. Two hedgehogs with respective charges q_a and q_b can combine to form hedgehogs with charge q_a+q_b or $|q_a-q_b|$. The radial hedgehog nucleated by a water droplet in a nematic has unit charge. Boundary conditions at infinity or at the outer surface of an enclosed region, such as a larger nematic drop, determine the total topological charge. A cell with parallel boundary conditions at infinity has zero charge. Thus the addition of a single spherical particle with normal anchoring must nucleate an additional unit charge hedgehog out of the nematic itself; this combines with the radial hedgehog of the droplet to produce total charge zero. A zero charge can be achieved if the second point defect is a hyperbolic hedgehog, as depicted schematically in Fig. 2. The full droplet-defect assembly forms a topological dipole. Unlike an isolated droplet of unit charge, this assembly satisfies the global boundary conditions imposed on the sample, since the director is homogeneously aligned far from the dipole.

Other topological defects can satisfy the requirements that the total topological charge be zero. One such defect is a disclination line, called a Saturn ring, shown in Fig. 3

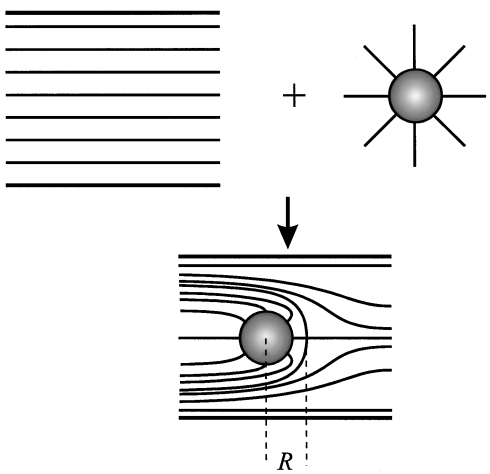

FIG. 2. Formation of a hyperbolic hedgehog as a particle with normal boundary conditions is introduced in a homogeneously aligned liquid crystal. This defect allows the director to be aligned along the z axis (horizontal axis) far from the particle. The droplet-defect pair has a total topological charge of zero, and dipolar symmetry.

[10,15]. Such a disclination ring is located around the particle; its axis is aligned along the axis of alignment of the nematic in the far field. This configuration also satisfies the global topological charge constraint. The exact configuration chosen by the system is the one that results in the lowest elastic energy. We find experimentally that the hedgehog is more stable than the Saturn ring. This behavior can be understood by using an ansatz for the director field that allows the continuous transformation from a hedgehog defect into a Saturn ring to be described [16].

A radial sphere of nematic liquid crystal, such as occurs in multiple emulsions, presents different global boundary conditions [17]; here the total topological charge must be unity, and particles confined within such a sphere must satisfy this condition [6]. Thus, as depicted in Fig. 4, there is no additional topological defect associated with a single particle with homeotropic anchoring, as it directly fits the radial configuration of the large host sphere. However, introduction of

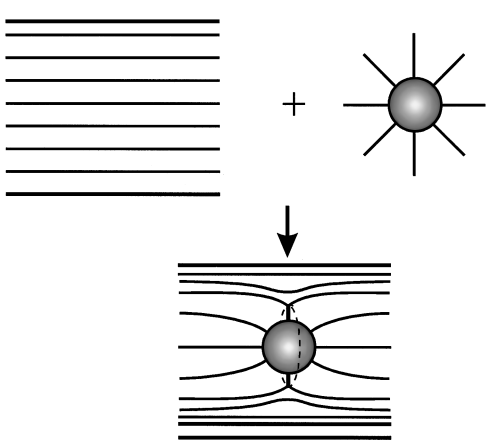

FIG. 3. Schematic of the director field of a Saturn ring, a disclination loop of strength $-\frac{1}{2}$, whose axis is aligned along the z axis (director axis in the far field). The total topological charge is zero.

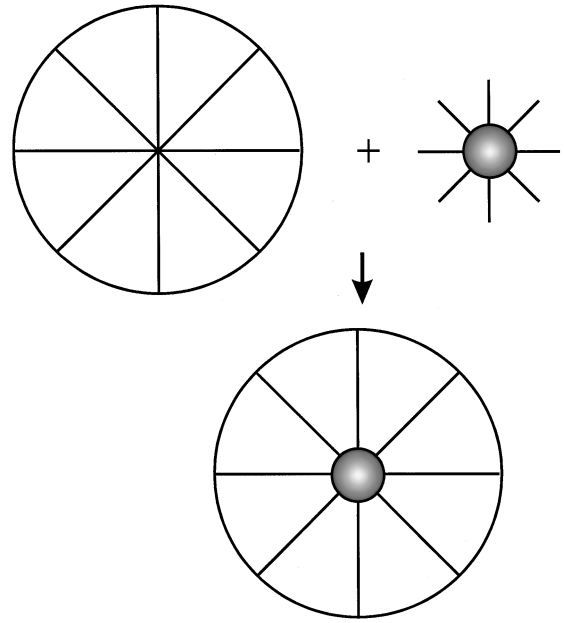

FIG. 4. Director field in a empty drop of liquid crystal (top left). The normal boundary conditions lead to a radial configuration and to the formation of a radial hedgehog in the center of the drop. In contrast to the case of a homogeneously aligned sample, a small particle with normal boundary conditions can be introduced in the large drop, without formation of any additional defect (bottom).

k additional droplets results in the formation of k additional hyperbolic hedgehogs. We note that this implies that there must always be exactly one fewer defect than particle; by contrast, for homogeneous alignment, there must always be exactly as many defects as there are particles.

When the anchoring on a particle is planar, a tangential configuration is expected [18]; this structure is depicted in Fig. 5. The boundary conditions are met by the creation of two surface defects, called boojums [19,20], located at the poles of the particles. They are diametrically opposed, and aligned along the axis of the nematic phase. This allows the far field director orientation to be homogeneous as required by the global boundary conditions.

A more quantitative account of the behavior of the liquid crystal, and the topological defects that result upon addition of particles, can be obtained by considering the free energy of the system. The elastic distortions in a nematic liquid crystal are known as splay, twist, and bend deformations [7,8]. The resultant elastic free energy density F, called the Franck free energy, is

$$F=\tfrac{1}{2}K_1(\nabla\cdot\mathbf{n})^2+\tfrac{1}{2}K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+\tfrac{1}{2}K_3[\mathbf{n}\times(\nabla\times\mathbf{n})]^2 \tag{1}$$

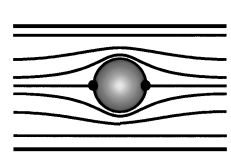

FIG. 5. A particle with planar boundary conditions in an aligned liquid crystal. Two surface defects known as boojums are induced on the surface of the particle.

where K_1, K_2, and K_3 are the splay, twist, and bend moduli, respectively. The director fields adopted in each of the situations described above can be determined by integrating over the volume, and minimizing F with the appropriate boundary conditions. Unfortunately, an exact calculation is very difficult. Instead it is possible to use a different approach, based on an analog to electrostatics [6,16,18,21]. We restrict our consideration to the limit of the assumption of a single elastic constant, and set $K_1=K_2=K_3=K$. An approximate form, up to a scaling factor, of the director field far from the particle can be derived, since minimization of F requires that the far-field transverse components of the director, n_x and n_y, where the z axis is taken as the axis of alignment, are solutions of the Laplace's equation [21]. The transverse components can thus be treated as two components of a Coulomb field in which the particles are elementary multipolar sources. The lowest order multipolar term that is relevant is determined by the symmetry of a particle-defect assembly. For example, the particle-hedgehog assembly (Fig. 2) has a dipolar character [6], while both the droplet-Saturn ring (Fig. 3) and the tangential structure (Fig. 5) have a quadrupolar character [18].

A more complete description of the director field of the topological dipoles can be obtained by using an *Ansatz* that equates **n** to the electrostatic field resulting from a charged conducting sphere in a uniform electric field [6,16]. Both fields satisfy the same boundary conditions; they are normal to the surface of the particle, and aligned along the z axis at infinity. This *Ansatz* allows the short-range, local structure to be predicted, and the separation between a droplet and its companion defect R to be determined: it suggests that $R=1.19a$; an example of this spacing is shown in Fig. 2. This *Ansatz* also allows the determination of the value of the scaling factor in the expressions for the far-field transverse components of the topological dipoles deduced from the Laplace's equation. Recently, a second, more general, *Ansatz* for the topological dipoles was introduced to study the stability of hedgehogs defects versus Saturn rings [16]. This new *Ansatz* also predicts slightly different behavior for the structure of the dipole; for example, it suggests that $R=1.26a$, a value that is slightly larger than the simpler *Ansatz*. In addition, the scaling factors for the long-range interaction between the particles are different, although they are of the same order of magnitude.

Once the topological configuration around an isolated particle is known, the interactions between the particles can be investigated. Predictions of the long-range interactions can be determined analytically through integration of a free energy density containing F, plus terms allowed by symmetry which couple the director and its distortions to the concentration of particles [6,16,18]. From the approximate forms of the director field obtained within the electrostatic analogy, we expect that the particle-hedgehog pair behaves qualitatively as a dipole at long range, and that the tangential particles or droplet-Saturn ring assemblies behave qualitatively as quadrupoles. From symmetry the long-range interactions can be predicted up to a scaling factor. This scaling factor can be determined if n_x and n_y are known quantitatively; this has been done by using the *Ansatz* to describe the director field around topological dipoles [6,16]. The lowest order term of the expression for the long-range interaction energy U between two topological dipoles located at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ is

$$U \approx -4\alpha\pi K a^4 \left(\frac{1-3\cos^2\theta}{d^3} \right) \tag{2}$$

where $d=|\mathbf{r}_\alpha-\mathbf{r}_\beta|$, θ is the angle between $(\mathbf{r}_\alpha-\mathbf{r}_\beta)$ and the z axis, and α is a factor which depends upon the *Ansatz* used. For the first *Ansatz* within the electrostatic analog [6], $\alpha \approx 9$, while, for the second *Ansatz* [16], $\alpha \approx 4.8$. Both models predict a dipole-dipole interaction which, for interactions that are strong enough, results in the formation of chainlike structures in which the dipolar droplet-defect assemblies point in the same direction.

For the quadrupolar case, the expression for the interaction energy is [18]

$$U \propto K \frac{a^6}{d^5} (9-90\cos^2\theta+105\cos^4\theta). \tag{3}$$

This interaction is attractive when the line joining the particle centers makes an angle between 31° and 70° to the z axis; the maximum attraction occurs when the angle is about 49°. The particles repel each other when they are oriented in other directions. Therefore, the structures generated by quadrupolar interactions will be significantly different from those generated by dipolar interactions; this demonstrates the critical importance of the anchoring conditions, and of the resultant topological structures around isolated droplets.

Although elegant, the electrostatic analog has its limitations. First, it assumes only a single elastic constant; by contrast, the elastic constants are different for real liquid crystal materials, even though they are of the same order of magnitude. Second, the electrostatic analog is only valid at long range. At short range, more complex phenomena can govern the behavior and the structures of the particles. Nevertheless, despite its shortcomings, the electrostatic analog is a very useful picture which provides qualitative guidelines and quantitative predictions.

III. EXPERIMENTAL SYSTEMS

The colloidal particles used in this work are water droplets suspended in thermotropic liquid crystals. Such liquid-liquid dispersions are known as emulsions [22,23]; as with isotropic fluids, they are metastable and require energy to be formed. This energy is required to provide the large interfacial energy associated with the production of small particles. However, in anisotropic fluids, an additional contribution arises from the distortions of the order of the solvent surrounding the particles [5]. These elastic distortions, which are of the order Ka per droplet, make the dispersion process more costly energetically than in isotropic fluids.

The energy required to produce the water droplets is supplied mechanically by vigorously shaking the sample which is initially composed of the two fluids, each of which has a low viscosity. The energy supplied is sufficient to overcome both the interfacial and the elastic energies required to suspend the small water droplets. To prevent their recombination or coalescence, amphiphilic compounds are used. In a fashion similar to classic emulsions [22,23] composed of iso-

TABLE I. List of systems used, including composition, anchoring, and type of emulsions. The liquid crystal materials were provided by E. Merck Industries. The ratio K_3/K_1 is given by the manufacturer, except for the 5CB and $K15$ for which the ratio K_3/K_1 is taken from Ref. [3].

Sample	Liquid crystal	Amphiphilic compounds	Approximate water amount	Anchoring	Emulsion type	Ratio K_3/K_1
1	5CB, $K15$	Tween 60	20% or less	normal	inverted	1.56
2	5CB, $K15$	Tween 60	more than 30%	normal	multiple	1.56
3	5CB, $K15$	SDS	from 30% to 50%	normal	multiple	1.56
4	5CB, $K15$	PVA	5%	planar	inverted	1.56
5	ZLI2620	PVA	5%	planar	inverted	0.73
6	ZLI2248	PVA	5%	planar	inverted	1.13
7	ZLI4747	PVA	5%	planar	inverted	1.26
8	ZLI4330	PVA	5%	planar	inverted	1.46
9	ZLI1132	PVA	5%	planar	inverted	1.95

tropic oil and water, these compounds are adsorbed at the water–liquid-crystal interface, and impart stability against coalescence to the particles. It is known for classic emulsions that certain compounds are more suitable to stabilize water droplets in oil (direct emulsions) while others are more suitable to stabilize oil droplets in water (inverted emulsions). It is also commonly recognized that amphiphilic compounds which are soluble in the continuous phase tend to provide better stability of the droplets. This knowledge can help in choosing the amphiphilic compounds used to stabilize water droplets in liquid crystals. However, in liquid crystal systems, the adsorbed compounds also serve an important function in addition to stabilizing the droplets; they also allow the boundary conditions of **n** to be controlled. Indeed, the interactions between the interfaces and the liquid crystal molecules determine the strength and the nature of the anchoring of the liquid crystal. This critical property imposes additional constraints in the choice of the amphiphilic compounds; however, the anchoring properties known for different systems can also provide guidance in the choice of suitable compounds [4,9].

From extensive studies of liquid crystal droplets dispersed in water (direct emulsions), some compounds leading to strong normal or planar anchoring are well known [4]. We have used these properties as a starting point for the formulation of our inverted nematic emulsions. For example, polymers such as polyvinyl alcohol provide planar anchoring of thermotropic liquid crystals at water interfaces, while several molecular surfactants can provide normal anchoring. Although the curvature is in the opposite direction in inverted systems, this information is nevertheless relevant, because anchoring is a molecular phenomenon which should not depend strongly on the curvature of the interfaces, the surface of a micrometer-sized droplet being essentially flat at the molecular scale.

The systems used are tabulated in Table I. To obtain systems with normal anchoring, molecular surfactants are employed: polyoxyethylene sorbitan monostearate (Tween 60), sorbitan monooleate (Span 80) and sodium dodecyl sulfate (SDS). With isotropic oils, Span 80 is used to stabilize inverted emulsions (water in oil), while SDS is used to stabilize direct emulsions (oil in water). Tween 60 has intermediate properties and, depending on the oil, can be used to stabilize either inverted or direct emulsions. We have observed that Tween 60 is soluble in the liquid crystal used. It is therefore a good candidate for making stable inverted emulsions with normal anchoring. By mixing about 20% (or less) of water and liquid crystal with a small amount of Tween 60 (0.1%), we observe the formation of a stable inverted emulsions. When samples prepared by this procedure are observed between crossed polarizers, pronounced birefringence patterns around the droplets are noted. These patterns are described below, but they immediately indicate that the droplets are successfully suspended in the nematic phase, and that they impose distortions of the nematic director field, as expected in limits of strong normal anchoring.

Addition of more water in such systems to get more concentrated suspensions leads to the formation of multiple emulsions composed of micrometer-sized water droplets dispersed in large liquid crystal drops of several tens of microns, which are themselves dispersed in a continuous aqueous phase. The anchoring of the liquid crystal molecules is normal at the internal surface of the large liquid crystal drops and at the external surfaces of the small water droplets. The resultant large nematic drops have a radial configuration [6,17]. A key to the stability of the multiple emulsion is the stability of the large liquid crystal drops in water; this stability is provided by the use of Tween 60.

In order to obtain more concentrated inverted systems while avoiding the formation of multiple emulsions, we mix Tween 60 with Span 80. With such a surfactant mixture the large liquid crystal droplets in water are much less stable, and the tendency to form multiple emulsions is reduced. However Span 80, unlike Tween 60, is not soluble in the liquid crystals used here. From its poor affinity for the continuous phase, Span 80, when used alone or when mixed in a large ratio with Tween 60, leads to a strong adhesion between the droplets and to poor stability of the water droplets. Such adhesion phenomena are known in classic emulsions [24,25]; they are avoided in the present study since they obscure the structures of interest.

Surprisingly, we have observed that multiple emulsions can also be formed by using SDS, while still retaining the condition of normal anchoring provided by molecular surfactants. With isotropic oils, SDS is known to stabilize only oil droplets in water. By contrast, in nematic oils, it can also stabilize small water droplets inside larger liquid crystal droplets for several weeks. As discussed below, the origin of

this unexpected stability is the distinctive anisotropy of a nematic oil.

Stable direct emulsions with planar anchoring can be produced by using polyvinyl alcohol (PVA), a polymer which is soluble in water. This polymer is insoluble in oils, and is inefficient at stabilizing inverted emulsions. Nevertheless, we have formulated inverted nematic emulsions by using this compound in the presence of small amount of water (Table I). An aqueous solution containing 1% PVA is first prepared, and then vigorously mixed with the liquid crystal. Although PVA preferentially stabilizes direct emulsions, an inverted one is formed because the amount of water is too small to form the continuous phase. The resultant emulsion has a short lifetime of only a few minutes; however, this is sufficient to study the properties of the emulsion. We observe birefringence patterns around the droplets, indicating that the anchoring is strong and planar, as desired. Moreover, the time for coalescence is sufficiently long to observe isolated droplets with planar anchoring and the formation of small clusters, the structure of which is described in Sec. IV. Thus these systems are useful to probe the essential features of the elastic interactions. However, more investigation is required to identify other amphiphilic compounds which provide both planar anchoring and greater stability of the droplets.

IV. ISOLATED WATER DROPLETS IN LIQUID CRYSTAL

Birefringence patterns around isolated water droplets allow the director structure to be determined, and the accompanying topological defects to be identified. These patterns are observed with optical microscopy by using crossed polarizers. To make the analysis simpler, the global liquid crystal alignment must be controlled. Thus we place the samples between polyimide coated glass slides which are rubbed to induce planar anchoring of the liquid crystal molecules at the glass surfaces. The resultant director is homogeneous and parallel to the surface of the slides; the direction of the induced alignment is taken as the z axis. In all our experiments, the thickness of the sample was about 30 μm, ensuring that good photographs of the structures could be obtained; however, similar behavior was observed up to the maximum thickness that the objective allowed, about 100 μm. The size of the samples was always much greater that the thickness, and was of order 1 cm across. These sample sizes were always much larger than the small water droplets, ensuring that the boundary conditions were set essentially at infinity. We can thus investigate the behavior for different anchoring conditions at the interfaces of the water droplets. All experiments reported here were performed at room temperature.

A. Normal anchoring

The birefringence pattern around an isolated droplet, stabilized with Tween 60, is shown in Fig. 6. A well-defined cross is observed near the particle. The center of the cross and the center of the droplet are aligned along the z axis, and hence along the global direction of **n**. Far from the particle the background is dark, indicating that the director is aligned along the z axis as required by the boundary conditions imposed by the glass slides. The observed pattern corresponds to the structure of the topological dipole depicted in Fig. 2;

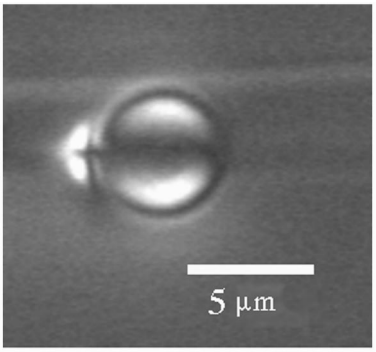

FIG. 6. Optical microscope picture, using crossed polarizers, of a water droplet with normal boundary conditions suspended in an aligned liquid crystal. The cross near the surface to the left of the droplet is a hyperbolic hedgehog. The background of the picture is uniformly dark, indicating that the liquid crystal is aligned along the horizontal axis far from the particle, as expected from the association of a particle and a hyperbolic hedgehog. This assembly forms a topological dipole.

the small cross is the hyperbolic hedgehog defect [26] that must be induced in the liquid crystal to ensure global conservation of topological charge. This pattern is always observed in our experiments, confirming that the anchoring of the liquid crystal on the surface of the droplet is normal, as expected. (We note that it is conceivable that the angle is not perfectly normal; we would not be able to distinguish very small deviations.) Moreover, it confirms that the hyperbolic hedgehog, rather than the Saturn ring, is the lowest-energy defect that compensates for the topological charge of an isolated particle in homogeneously aligned liquid crystal. The observed separation between the defect core and the droplet is a small fraction of the droplet radius, a. From optical microscopy observations, we estimate that $R/a = 1.2 \pm 0.1$, where R is the distance between the defect core and the center of the particle. This is in good agreement with the predictions of the two *Ansätze* that were proposed to describe the director field of the topological dipoles [6,16].

B. Planar anchoring

Planar anchoring on the droplets is obtained by adding PVA to the water phase. An isolated droplet stabilized with PVA is shown in Fig. 7. As in the case of normal anchoring,

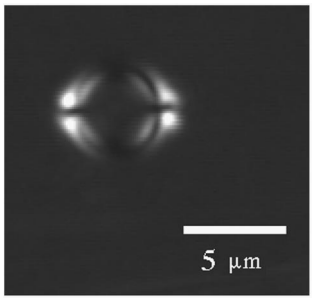

FIG. 7. Optical microscope picture, using crossed polarizers, of a water droplet with planar boundary conditions suspended in an aligned liquid crystal. The two bright regions located on the surface of the droplet indicate the presence of surface defects known as boojums. These defects are aligned along the alignment axis of the liquid crystal, which is along the horizontal axis.

the background is dark far from the particle. However, the topological constraints are no longer satisfied by a single defect. Instead, two strongly birefringent regions, diametrically opposed and aligned along the z axis, are observed. These represent a pair of topological point defects, known as boojums [19,20], at the poles of the droplets. The tangential structure of the director field corresponding to this system is depicted in Fig. 5. In this case again, the experimental observation agrees with the topological structure expected. However, by contrast to the normal anchoring conditions, the droplet-defect assembly with planar anchoring has quadrupolar symmetry, and this modifies its interactions with neighboring droplets, as discussed in Sec. V.

V. COLLOIDAL INTERACTIONS AND STRUCTURES

In this section we describe the behavior of the colloidal droplets that results from interactions between the particles induced by the orientational elasticity of the liquid crystal host. Immediately after the sample preparation, isolated particles are observed; as time elapses these diffuse and are attracted to each other, forming larger clusters. The formation of these clusters confirms the existence of long-range attractive interactions between the particles which are induced by the elasticity of the liquid crystal phase. However, short-range repulsive interactions must also exist in some conditions, as the droplets can remain separated by a small fraction of their diameter. These repulsive interactions are a new form of colloidal stabilization. In all cases, the clusters have a well-defined anisotropic structure reflecting the distinct character of these colloidal interactions. In this section, we discuss three different systems which exhibit attractive interactions: inverted emulsions with normal anchoring in homogeneously aligned samples, multiple emulsions with normal anchoring, and inverted emulsions with planar anchoring in homogeneously aligned samples.

A. Inverted emulsions with normal anchoring

We describe the behavior of emulsions stabilized with Tween 60 in which water droplets are suspended in a continuous nematic phase. This surfactant stabilizes the droplets while maintaining normal anchoring conditions at their surfaces. The samples are placed between rubbed polyimide-coated slides which impose a homogeneous alignment of the continuous liquid crystal phase in the far field. Two droplets in a such sample are shown in Fig. 8. They are aligned along the z axis; there is a hyperbolic hedgehog between them, with a second hyperbolic hedgehog to their left. A typical example of the structure formed by a larger number of particles is shown in Fig. 9. Linear chaining of the particles is apparent; this is reminiscent of the behavior of colloidal particles in electrorheological or magnetorheological fluids [13]. In such fluids, the particles are polarized by an external electric or magnetic field, and they behave as dipoles subject to an attraction along the direction of the external field. In nematic fluids, there is no such external field; however, from the electrostatic analog, droplets with compensating hyperbolic hedgehog defects are expected to behave at long range like electrostatic dipoles. These should attract each other, forming long chains, exactly as observed. The corresponding structure of the director field is depicted by Fig. 10. It shows

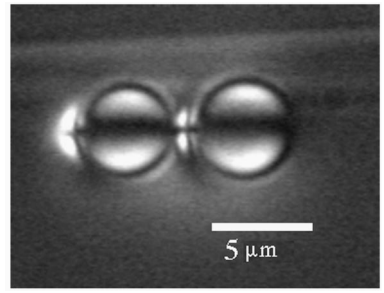

FIG. 8. Optical microscope picture, using crossed polarizers, of two water droplets with normal boundary conditions suspended in an aligned liquid crystal. The droplets are aligned along the alignment axis of the liquid crystal, which is along the horizontal axis. The direction of each dipole, defined by the direction from the center of the droplet to the core of the compensating defect, is the same. This leads to the presence of a hyperbolic hedgehog between the particles. The separation between the particle is a few tenths of a micrometer.

the hyperbolic hedgehog defects that exist between each of the particles, and the far-field uniform orientation of the director. The conservation of the topological charge requires that there be exactly the same number of hyperbolic defects as there are particles, with one defect corresponding to each particle. This is clearly observed for the two droplets in Fig. 8; inspection of the chain in Fig. 9 between crossed polarizers and under higher magnification confirms this behavior for the longer chains as well.

As time elapses, the linear chains diffuse through the sample and form larger aggregates with a more complex structure. An example of this is shown in Fig. 11; the linear nature of the interaction persists, but the chains become branched as they grow sufficiently long. Moreover, there continues to be exactly one hyperbolic defect per particle for these very large clusters. As the clusters become even larger, they tend to become more compact, as more branches develop. Thus, after a long time, the droplets no longer appear ''dispersed,'' but instead form large clusters. This helps account for the commonly observed apparent difficulty in suspending particles in nematic liquid crystal hosts; the elastically induced attraction causes the particles to form large clusters, making it difficult to fully disperse the particles.

The electrostatic analog correctly accounts for the anisotropic attractive interactions which lead to the formation of the chains. However, within the chain, the droplets do not touch each other, but rather remain separated by a few tenths of a micron. This separation s grows with the size of the colloidal particles and corresponds to about twice $(R-a)$, the separation between an isolated particle and its companion

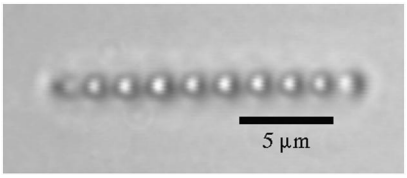

FIG. 9. Optical microscope picture of several water droplets suspended in an aligned liquid crystal. The droplets form a long chain that is aligned along the alignment axis of the liquid crystal, which is along the horizontal axis.

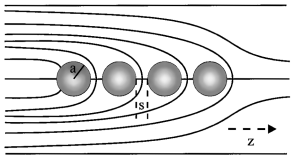

FIG. 10. Schematic representation of the director field for a chain of droplets formed by interaction between the topological dipoles. There are exactly as many defects as particles.

defect. This separation results from shorter range effects which are not described within the electrostatic analog. Nevertheless, this phenomenon can still be ascribed to the orientational elasticity of the liquid crystal. Indeed, such an equilibrium separation indicates a repulsion whose range is significantly larger than the range of repulsion observed with surfactant stabilization of water droplets in an isotropic oil, where the range of the steric repulsion is molecular.

This separation of a few tenths of a micrometer arises from the repulsive interaction caused by the fact that, between the particles, the director must change its orientation from vertical to horizontal in a distance on the order of $s/2$. This change results in $\nabla \mathbf{n} \approx 2/s$, leading to a considerable cost in elastic energy, as can be seen from the minimization of F in Eq. (1). This behavior has important consequences; it provides a completely new form of colloidal stabilization, since the droplets cannot come into contact and coalesce even while they approach along the direction of maximum attraction. Regardless of the usual surfactant properties that lead to emulsion stabilization in isotropic systems, this stabilization in the liquid crystal host is based only on the fact that the surfactant imposes normal boundary conditions in an anisotropic host fluid; it is completely different from the more usual forms of emulsion stabilization, which depend on the surfactant at the surfaces to provide the local surface repulsive forces. Moreover, since this phenomenon is induced by the ordering of the nematic liquid crystal, it can be switched off by heating the nematic into the isotropic phase. This transition allows the particles to diffuse freely without being attracted to each other, and to coalesce as they collide if the surfactant does not provide sufficient stabilization in the isotropic liquid crystal. This represents a controlled way to initiate fusion between particles, to regulate their mixing, and to induce localized physical or chemical phenomena.

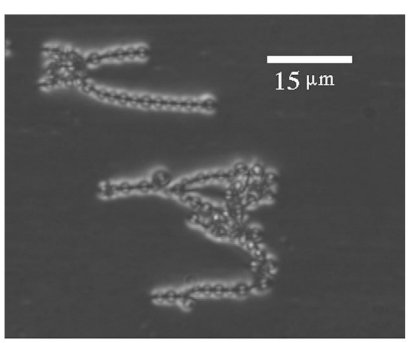

FIG. 11. Optical microscope picture, using crossed polarizers, of larger aggregates that are observed a long time after the sample preparation. Lateral connections between chains induce the formation of more complex structures. Nevertheless, the anisotropy of the interactions clearly persists.

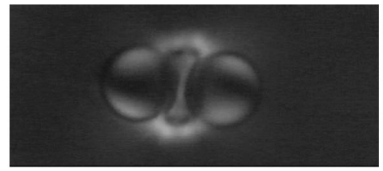

FIG. 12. Optical microscope picture, using crossed polarizers, of two water droplets in an aligned liquid crystal. The director is normal to the surface of the particles. However, the droplets do not form a pair of dipoles, each with a companion hyperbolic hedgehog, but are instead connected by two bright strings that indicate different distortions of the director field.

Our discussion up to this point has focused on droplets whose topological charge is compensated by an additional defect in the host liquid crystal. While this is the most commonly observed behavior, we do occasionally, but regularly observe a distinctly different structure for some pairs of droplets. Instead of having two compensating hyperbolic defects, one associated with each particle, the two droplets are observed to contact one another, with what appears as a bright, stringlike material connecting them; a typical example is shown in Fig. 12. Here the two droplets are viewed through crossed polarizers, and the strings appear as bright lines, joining the pair of droplets; moreover, there are no apparent hedgehog defects associated with each droplet and there is no evidence of any singularity of the director field. The exact configuration of the nematic director associated with this structure is not clear. It is conceivable that these strings represent localized distortions of the director, which may begin as localized hedgehogs or Saturn rings, but which then become elongated to form the strings observed. Alternatively, this pattern may reflect a cylindrical or tubular structure of the director field between the droplets, which appears stringlike when viewed under crossed polarizers. This may arise because of a continuous deformation of the director field in three dimensions between the two particles [16,27].

The existence of this structure, whatever its nature, demonstrates that a variety of metastable states can be accessed by particles suspended in anisotropic fluids. Very strong distortions are required to go from this state to the dipolar state, with the resultant barrier being much higher than $k_B T$. However, the mechanical energy supplied during the sample preparation is sufficient to access either state. The large barriers between the metastable states result from the anisotropy of the host fluid, and allow the particles to form these completely different structures; this behavior is in striking contrast with what is observed in an isotropic fluid.

B. Multiple emulsions with normal anchoring

Multiple emulsions can be formed by using SDS or Tween 60; these are composed of small water droplets dispersed in large liquid crystal drops which are themselves suspended in a continuous water phase. Both of these surfactants provide normal anchoring on the surface of both the large liquid crystal drops, as well as on the surface of the small water droplets. The multiple emulsions are formed by vigorous shaking of the sample. The size of the internal water droplets is typically between 1 and 10 μm while the size

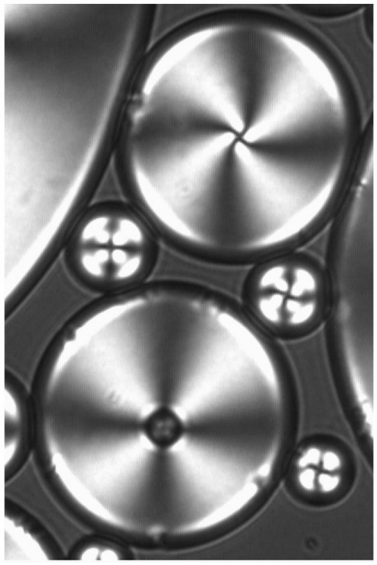

FIG. 13. Optical microscope picture, using crossed polarizers, of large liquid crystal drops suspended in water. The liquid crystal anchoring is normal to the internal surface of the drop. This leads to a radial configuration resulting in birefringence patterns that exhibit a characteristic dark cross. The large drop on the top is empty. A slight twist is observed at the center of the particle. The large drop on the bottom contains a small water droplet that is pinned near the center of the host liquid crystal drop. The anchoring of the liquid crystal is normal to the external surface of the small droplet. The droplet replaces the core of the hedgehog defect in an empty drop. Thus no additional defect is required to introduce the small droplet. We note the lack of twist as a small particle replaces the core of the radial hedgehog.

of the larger liquid crystal drops is typically several tens of micrometers; thus the shape of the larger drops is typically distorted somewhat as they are squeezed between the microscope slides. However, this distortion has little affect on the behavior of the smaller internal water droplets. The number of these internal water droplets, k, varies from one large sphere to the other.

An example of a large, but empty, liquid crystal drop is shown by the drop in the upper part of Fig. 13. The cross pattern-arises from the radial configuration of the nematic order within the drop when viewed through crossed polarizers. The faint ring around the large drop is due to optical interference. Whenever the nematic drop is empty, and does not contain smaller water droplets, the cross pattern adopts the curved structure apparent in the figure, which is known as a twisted radial [4]. The twist allows relaxation of some splay; the equilibrium structure results from competition between these deformations [4,16]. This competition does not occur locally, at the center of the nematic drop, when a single smaller water droplet is contained inside; then the cross pattern is straight, and no relaxation of splay is observed. This difference in appearance between the empty drops and those containing a single water droplet provides a convenient means of identifying the empty drops. An example of a nematic drop with a single water droplet is shown by the large drop in the lower half of Fig. 13. When there is only a single internal droplet ($k=1$), no additional topological defects are associated with the particle. Such a single droplet is pinned at the center of the radial drop [6], exactly

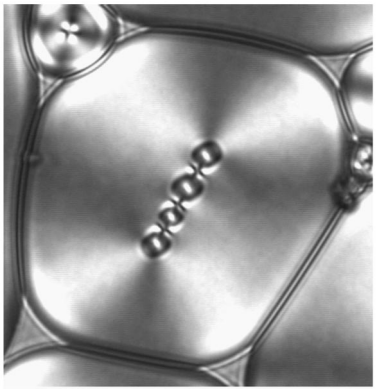

FIG. 14. Optical microscope picture, using crossed polarizers, of multiple emulsion which consists of a large liquid crystal drop in water. Inside the drop are four small water droplets. A hedgehog defect can be seen in the space between each particle. Thus there are exactly three defects associated with the four particles, as expected from the conservation of the topological charge.

like the core of the hedgehog defect that is located at the center of an empty nematic drop. The Brownian motion of the internal water droplet is essentially negligible, indicating that the elastic energy that is involved is much larger than k_BT. In such conditions, the droplet can not diffuse toward the surface of the large radial sphere, significantly increasing the stability of the water droplets. Indeed, as the internal droplet has no access to the surface of the large sphere, it has no opportunity to coalesce with the external water phase. However, when the liquid crystal is heated to the isotropic phase, the internal droplet is no longer subject to elastic forces, and the water droplets exhibit the Brownian motion common to colloidal particles; the droplets also then become somewhat unstable to coalescence when they collide with the walls of the liquid crystal drops.

The conservation of topological charge requires that, when k small droplets are introduced within the radial drops, $k-1$ topological defects must be formed. This is observed experimentally [6]. Moreover, as in the case of homogeneous alignment, the topological defects are hyperbolic hedgehogs. In this configuration, the small water droplets still form linear chains, and two neighboring particles are still separated by a significant fraction of their diameter, with a hyperbolic hedgehog between them, as shown in Fig. 14. The formation of chains cannot be directly ascribed to dipolar interactions as in the case of aligned samples, because of the different global boundary conditions. Nevertheless, both systems have fundamental similarities because the nature of the topological defects between the particles is similar. We illustrate this schematically in Fig. 15, where we show a chain of particles separated by hyperbolic hedgehogs. Thus the basic phenomena which lead to the separation between the neighboring particles, thus stabilizing them, are expected to be comparable in the radial and homogeneously aligned geometries. However, in the multiple emulsions, the separation between the small water droplets is $s \approx 0.6a$, for a between 1 and 10 μm [6]. This is slightly larger than the separation between the droplets in chains formed in homogeneously aligned liquid crystal.

The stabilization provided by this elastic repulsion can explain the surprising formation of a multiple emulsion with

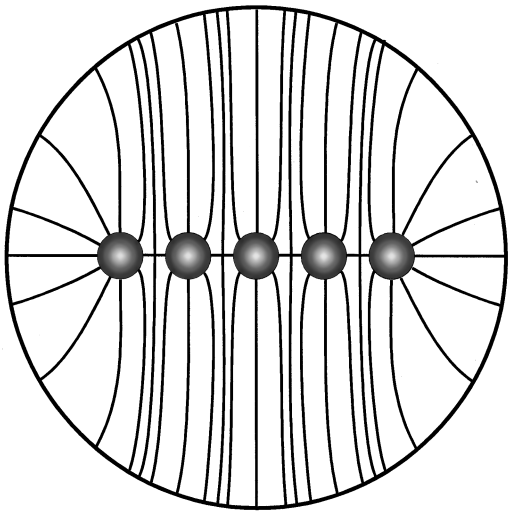

FIG. 15. Schematic representation of the director field in a multiple emulsion containing many small water droplets inside a large nematic drop. There is a hyperbolic hedgehog between each particles. Thus there are $k-1$ hyperbolic hedgehogs for k droplets.

SDS, a surfactant that is normally ineffective at stabilizing water droplets in an isotropic oil. Indeed, as long as the surfactant induces normal anchoring, the particles cannot approach too closely, since there is a hyperbolic hedgehog between them. Thus, even though the surfactant is not efficient at stabilizing the film between the droplets, they can nevertheless not coalesce. We can confirm that stabilization arises from the hedgehog defect induced in the liquid crystal, rather than from the surfactant, by heating an emulsion, made with K15 (Table I) and stabilized with SDS, above 35 °C, the nematic-isotropic transition temperature. In the isotropic phase, the droplets coalesce within an hour. By contrast, they remain stable for several weeks in the nematic phase. Thus, when heated to the isotropic phase, only a direct emulsion is stable, as expected for any emulsion composed of water, isotropic oil, and SDS.

C. Inverted emulsions with planar anchoring

The final group of experimental systems examined have parallel boundary conditions at the surfaces of the water droplets, which is achieved using PVA dissolved in the water phase. With these boundary conditions, the droplets form anisotropic aggregates, indicating that attractive interactions again result from the elastic distortions of the nematic liquid crystal. However, unlike the case of normal anchoring, the droplets come into contact with their neighbors at equilibrium. This indicates that there is no strong elastic repulsion, as is the case for normal anchoring. The stability of the contact droplets in contact is then presumably ensured by steric interactions provided by PVA. This accounts for why the droplets are poorly stabilized, since PVA is known to be inefficient at stabilizing water droplets in an oily compound. Thus the droplets coalesce after some minutes, and it is difficult to find very large aggregates. Nevertheless, examination of the samples immediately after preparation still provides ample time to investigate the nature of the attractive interactions by observing the small clusters formed from a few particles. As indicated in Fig. 16, the droplets are no longer aligned along the z axis, the direction of preferred orientation of n induced at the glass interface. Instead, a second particle attaches to the first in a region that is defined by the surface area of a cone, whose vertex lies at the center of the first particle and whose axis lies along the z axis, as illustrated schematically in Fig. 17. The line joining the centers of two particles forms an angle θ with respect to the z axis. Additional droplets are attached within the cone of any droplets in the cluster, resulting in the formation of more compact clusters. We can understand the origin of this structure by referring to the schematic picture shown in Fig. 17; the director is more uniform, and the distortions of n minimized, when the particles approach each other with the line joining their centers forming a nonzero angle with the z axis. When the particles are large enough, buoyancy forces tend to pack them against the glass slides, and, thus, the likelihood of observing chains increases, since the particles are confined to the surface of the cell. Focusing the microscope on this plane allows θ to be measured experimentally. For two particles of the same size, we find that θ is approximately 30°, as shown in Fig. 18. The value of this angle confirms this intuitive picture, since a straight line of the director field can be drawn tangentially to the second particle from one of the boojums near the first particle; this situation presumably corresponds to a minimum in the elastic energy.

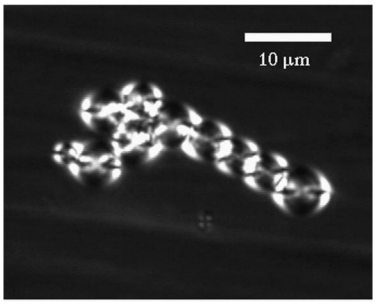

FIG. 16. Optical microscope picture, using crossed polarizers, of a cluster formed by several particles with planar anchoring suspended in an aligned liquid crystal. Neighboring particles are in contact, and form a well-defined angle with the alignment axis of the liquid crystal, which is along the horizontal axis.

At long range, the droplets with planar anchoring are expected to act as quadrupoles [18]. Thus their interaction should be repulsive when they are perpendicular ($\theta=90°$) or aligned ($\theta=0°$) along the z axis, and attractive for some

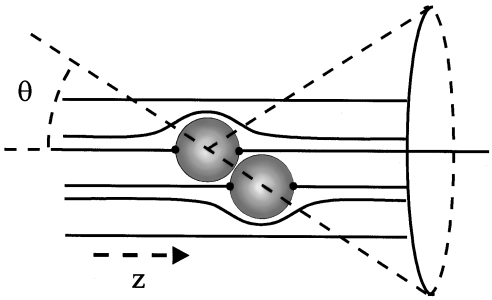

FIG. 17. Schematic representation of the nematic director field for two particles with planar anchoring that approach each other in an aligned liquid crystal. The particles make an angle θ with alignment axis of the liquid crystal, which is along the horizontal axis.

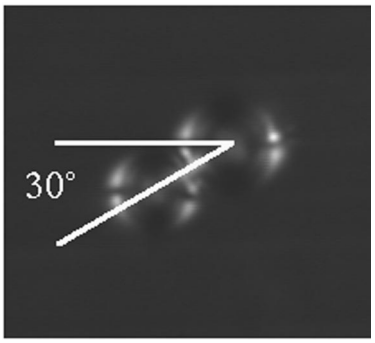

FIG. 18. Optical microscope picture of two equally sized particles with planar anchoring suspended in an aligned liquid crystal. The droplets are confined to the top surface of the sample, and make an angle of 30° with the alignment axis of the liquid crystal, which is along the horizontal axis. This angle does not depend on the nature of the liquid crystal used.

values of θ between 0° and 90°. However, according to the electrostatic analog, the angle for which long-range attraction is maximized is approximately 49° [18]. This theoretical value is different from the experimentally observed value for θ, this discrepancy is not surprising, since the theory is a long-range description that does not account for short-range effects.

Another possible origin of this discrepancy may be our assumption of a single elastic constant; in any real liquid crystal, the elastic constants are different. There is no calculation available that takes account of the three elastic deformations; however, it has been suggested that differences between the splay and bend moduli (K_1,K_3) can be accommodated by rescaling the x and y coordinates with respect to the z coordinates [18]. Therefore, the angle of maximum attraction would be expected to depend explicitly on the ratio of K_3/K_1. To investigate this possibility, we prepared six inverted emulsions using different liquid crystals, listed in Table I, where the ratio K_3/K_1 varies from 0.73 to 1.95. For all samples, we observed that θ remained constant at 30°. This demonstrates that the ratio K_3/K_1 is not the origin of the discrepancy between the theory and experiments. Therefore, the origin of the observed behavior must be ascribed to short-range effects not explicitly included in the theory. The behavior at longer range is also still uncertain; the angle of maximum attraction may differ from that at short range, and is perhaps closer to the one predicted by the electrostatic analog. Moreover, the dependence of the long-range interaction potential upon the elastic constants is as yet unknown.

VI. CONCLUSIONS

The results reported in this paper show clearly that many new phenomena are observed when colloidal particles are suspended in a nematic solvent. The interactions between the particles are governed by the orientational elasticity of the suspending fluid. These interactions lead to anisotropic structures which depend sensitively on the nature of the anchoring and on the global boundary conditions.

By using inverted and multiple emulsions with thermotropic liquid crystals, we have examined these interactions in a nematic solvent for two limits of strong anchoring; the normal and parallel conditions. At long range, these interactions have an elegant analog to electrostatics, providing a conceptual basis by which the origin of the observed behavior can be understood. At short range, the elastic interactions determine the local structures of the assembled particles, and can generate a repulsive interaction between them, thereby resulting in a new form of colloidal stabilization. Emulsions are ideal systems to use for these experiments; because the droplets are fluid, their interfaces are inherently more uniform, leading to more uniform anchoring of the liquid crystal. Moreover, the anchoring can be easily controlled through the physical adsorption of compounds which, by design, can be chosen to interact in different ways with the liquid crystal molecules. Finally, the use of a thermotropic liquid crystal with large elastic constants gives rise to strong forces which dominate the effects of entropy and other colloidal forces such as van der Waals forces. This greatly facilitates the study of the properties of the elastic forces. While many effects are studied in this work, we expect still more unusual phenomena to be observed as the full phase space of particle size, elastic constants, anchoring energies, and boundary effects are explored.

ACKNOWLEDGMENTS

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