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Interactions between colloidal inclusions in two-dimensional smectic-C^* films

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We report an experimental study of colloidal inclusions in free-standing films of smectic-C^* liquid crystal. The inclusions are cholesteric droplets that form above the bulk smectic-C^*-cholesteric transition temperature. Each droplet confined in a two-dimensional (2D) system, is accompanied by a topological defect. The distortions of the in-plane orientational order of the smectic-C^* film induce elastic interactions between the droplets. As in 3D water nematic emulsions, a short-range repulsion and a long-range dipolar attraction govern the stability of the inclusions and lead to their organization in chainlike structures. Our results are in agreement with recent theoretical predictions.

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Theoretical predictions [1] have been recently proposed to describe the behavior of particulate inclusions in two-dimensional systems that exhibit an orientational order. These predictions should be relevant for a wide range of systems ranging from Langmuir films composed of tilted rigid molecules at the air-water interface [2] to phospholipid bilayers [3,4] through two-dimensional films of smectic-C or C^* liquid crystals [1]. These latter systems are composed of stacked layers in which the molecules are tilted along a preferential direction [5]. Topological defects associated with the inclusions and elastic interactions between the inclusions are among the most important expectations. These interactions are expected to play a critical role in the stability of the inclusions and to lead to ordered structures in two dimensions.

In this paper, we study cholesteric (N^*) inclusions in smectic-C^* (SmC^*) membranes. These films serve as an experimental model for two-dimensional systems and allow theoretical predictions to be tested. By using optical microscopy between crossed polarizers we experimentally investigate the behavior of the N^* droplets in the membranes. A topological defect appears simultaneously with each particle nucleation. Kinetic analysis of the motion of the defect-particle pairs reveals long-range attractions between the inclusions. The involved interactions arise from the in-plane orientational elasticity of the film and cause the particles to form long chains. This behavior reflects the dipolar character of the defect-particle assemblies. The presence of a companion defect between neighboring particles induces a short-range repulsion that prevents the N^* droplets from coalescing. The present observations, which are reminiscent of the behavior of colloids in three-dimensional nematics, are in good agreement with recent theoretical predictions [1].

The used compound is the $n=11$ member (11BSMHOB) of the homologous chiral series in which n vary from 7 to 12 [6]. In bulk, the 11BSMHOB material exhibits the following phase sequence: Crystal (56.5 °C) SmC^* (106.1 °C) N* (123.9 °C) isotropic. As most of smectic liquid crystals, the SmC^* phase of 11BSMHOB can form films freely suspended across a hole in a glass or a metal plate [7]. The obtained membranes consist of an integer number of molecular smectic layers arranged parallel to the two free interfaces. In the SmC^* phase, each layer is a two-dimensional anisotropic liquid with rodlike molecules tilted in a preferential direction. The tilt angle θ is the angle between the long molecular axis and the layer normal z. The in-plane orientational order of the molecules in the smectic layers is specified by the so-called **c** director: the projection of the mean direction of the long molecular axis onto the layer plane. Chirality of the molecules induces an helical rotation of the **c** director along the z axis. This helical twist of the SmC^* phase is characterized by the pitch helix value P_0. The N^* phase can be described as a twisted nematic [5] in which the molecules exhibit only orientational ordering with a long-range rotation of the mean direction of the molecular long axis. Particular features of the used material are both the SmC^*-N^* phase transition and the large value of θ in the smectic phase (about 45°). The tilt angle is quasitemperature independent and always displays a value of 45° at the SmC^*-N^* phase transition. Such a tilt induces a pronounced orientational anisotropy in the smectic layers. The SmC^* pitch helix varies from about 0.4 μm at 80 °C to 0.73 μm at the SmC^*-N^* phase transition. More detailed physical properties of selected compounds from this series have been published elsewhere [6].

Films are prepared by drawing a small amount of liquid crystal in the SmC^* state across a 2.5-mm radius hole (R) in a steel plate. The thickness (e) of the studied films ranges from 0.1 to 0.5 μm. The film texture is observed between crossed polarizers with an optical microscope (Olympus BX 60) either in reflection or transmission mode. The present films achieve the ratio $e/P_0<1$. Their textures vary from dark to bright according to the position of the **c** director with respect to the polarizers. Thus, as a first approximation, we neglect the helical rotation of the **c** director along the Z axis in the texture analysis. Nucleation of droplets within the film appears a few degrees above the bulk SmC^*-N^* transition temperature. The same thermal process is used in every experiment: the smectic films are heated from 100 °C at a rate

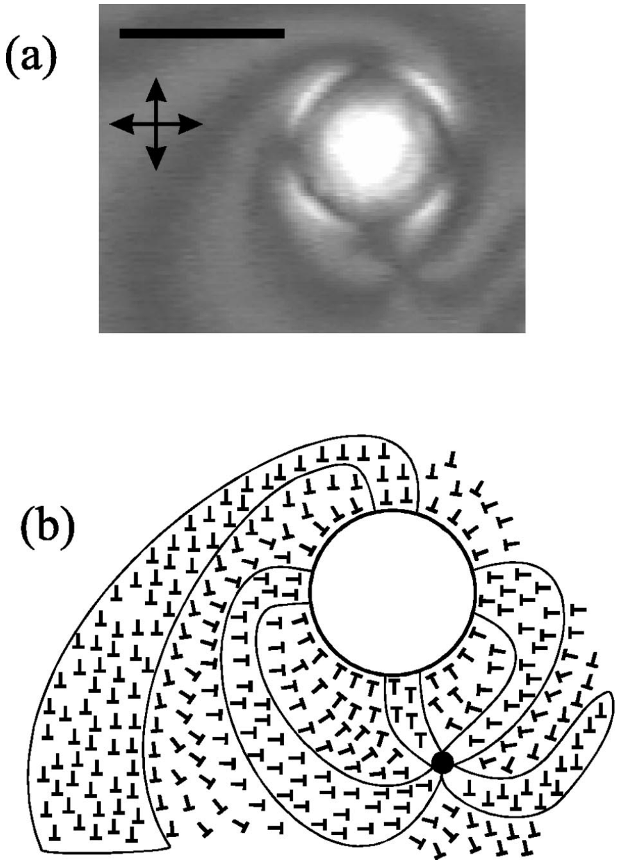

FIG. 1. (a) Microscope picture, in transmission between crossed polarizers, of the droplet with its associated four-armed star of alternating dark and bright regions (black bar: 10 μm). (b) Schematic configuration of the **c** director mapped from the microscope image. This associated defect is called ''hyperbolic point disclination'' due to the configuration of the **c** director around the point defect.

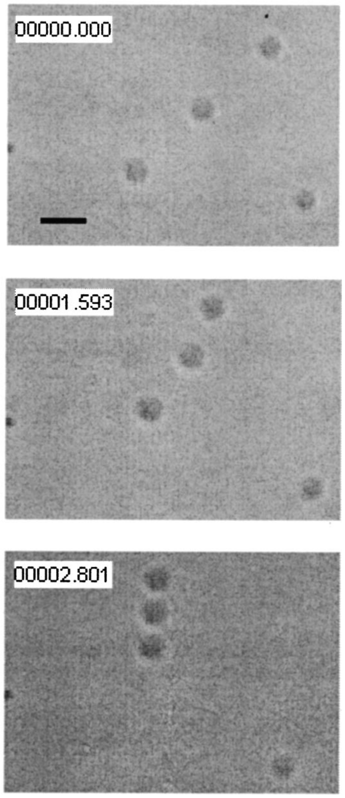

FIG. 2. Microscope picture of droplet chaining as a function of time (black bar: 10 μm). At $t=0$ s the separation between the droplets is several times their size. Elastic interaction pulls the droplets together; at $t=2.801$ s the three droplets have reached their equilibrium distance.

of 2 °C/min; the temperature is stabilized as soon as droplets appear. The temperature shifts between the nucleation of droplets and the bulk SmC^*-N^* transition strongly suggest that the local order in the droplets is cholesteric (a shift of 3° is readily obtained). Those shifts increase with decreasing film thickness. The droplet sizes range typically from 5 to 10 μm. But such large sizes do not hinder the stability of our SmC^* films. So far, nucleation of droplets in smectic free-standing films has only been reported in materials exhibiting a smectic A-isotropic or smectic A-N phase transition [8,9]; in these cases, the droplets remain randomly located because of the lack of anisotropy in smectic-A layers. The stability of the present films is probably ensured by a few smectic layers on the two liquid crystal-air interfaces; these layers box in the N^* droplets. Indeed, the surface tension associated with the sample-vapor interface is known to promote the smectic order at the surface [10,11]. Observations of the film texture between crossed polarizers reveal particular distortions of the **c** director around the particles. As shown in Fig. 1(a), a distorted four-armed star of alternating dark and bright regions is located close to each particle. The four dark branches are connected to the N^* droplet boundary. The **c** director mapped from our observations is shown in Fig. 1(b). The particle, around which the **c** director adopts normal boundary conditions, plays the role of a topological defect known as radial point disclination [''radial hedgehog'' in a three-dimensional (3D) system]. The associated topological defect close to the inclusion is known as a hyperbolic point disclination (''hyperbolic hedgehog'' in a 3D system) [12]. Association of a hyperbolic point disclination with a particle allows the **c** director to be homogeneously aligned far from the defect-pair assembly, minimizing thereby the Frank elastic energy associated with the in-plane distortions of the **c** director [1]. Disclinations can be characterized by a positive or negative integer topological charge [13,12]. Hyperbolic and radial point disclination having, respectively; a -1 and a $+1$ topological charge, the droplet-defect pairing allows the net topological charge of the film to be conserved and equal to zero. The droplet-defect pairs, as in nematic fluids, have a dipolar symmetry [14,1]. According to recent theoretical predictions [1], elastic interactions resultant from distortions of the **c** director are also expected to exhibit a dipolar character. This important feature is clearly confirmed experimentally. Indeed, the droplets do not remain randomly located in the film. Instead, they attract each other at long range and organize in chainlike structures. No free isolated droplets are longer observed a few minutes after their formation. Figure 2 illustrates both the anisotropy and the particularly long range (several times the droplet size) of the attractive forces be-

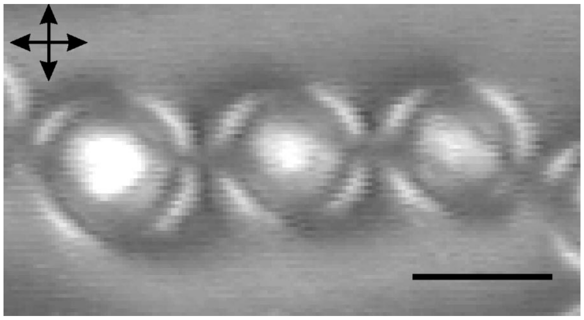

FIG. 3. Microscope picture, in transmission under crossed polarizers, of three droplets at equilibrium. The associated hyperbolic point disclinations prevent the contact, and so the coalescence (black bar: 10 μm).

tween particles. The dipoles in the chains have same direction and a hyperbolic point disclination is located between two neighboring particles (see Fig. 3). The presence of the defect prevents the N^* droplets from contacting each other. It acts as a repulsive barrier against coalescence of the particles. As shown in Fig. 4, at long time, very long chains can be observed in the film. Such droplets chains always exhibit the same number of defects as droplets. So is fulfilled the zero total charge brought out by homogeneous alignment in the far field.

In the theoretical analysis by Pettey and colleagues [1], the inclusions consist of circular islands containing additional smectic layers; each inclusion nucleates a companion topological defect. These island-defect pairs are modeled as topological dipoles within the context of a one-coupling constant approximation to the 2D Frank free energy. Our experimental system is similar in terms of topological analysis even if the type of the inclusion differs. Thus, we confront our experimental results to these theoretical predictions. The distance d between the associated defect and the center of an isolated droplet is expected to scale as $d=\sqrt{2}\ r$ (A) where r is the droplet radius. Although performed for a rather restricted range of particles radius, our experimental observations lead to $d/r=1.4\pm0.1$, in good agreement with the predicted value. To our knowledge, there is not yet a theoretical prediction concerning the separation between droplets. Nevertheless, one can expect this separation to scale with the droplet radius as the distance between defect and isolated particles. To check this hypothesis, we measured the distance D between centers of neighboring droplets as a function of their average diameter d_a [$d_a=(d_i+d_{i+1})/2$, d_i and d_{i+1}: droplet diameters]. As expected (see Fig. 5), a linear relation fits the data on the present experimental range. The slope of this linear dependency is 1.3 ± 0.1. This value is in agreement with the intuitive expectation that the separation between droplets should be close to $D=\sqrt{2}\ d_a$ resulting from the relation (A). Both the droplet-defect distance and the orientation of the dipole are expected to exhibit thermal fluctuations [1]. The theoretical angular and positional fluctuations are, respectively, given by $\langle(\delta\phi)^2\rangle=(1/2\pi n)\log(R/r)$ (where n is the number of layers of the film and R the system size) and $\langle(\delta d/d)^2\rangle=1/8\pi n$. Experimentally, slight angular fluctuations of about a few degrees are clearly observed. This is in good agreement with the theoretical expectations; indeed, with a system size (hole radius R) of about 2.5 mm, a droplet radius (r) of 2.5 μm, and a typical number of layers (n) equal to 100, the estimated value of $\delta\phi$ is about 6°. By contrast, we are not able to detect any significant fluctuations of d. This again agrees with the expectations. Indeed, for the used films, the amplitude of such fluctuations is expected to be smaller than a few microns, a distance lower than the optical microscope resolution. More quantitative measurements of both angular and positional fluctuations are under study. They need the use of much thinner films than those presently reported.

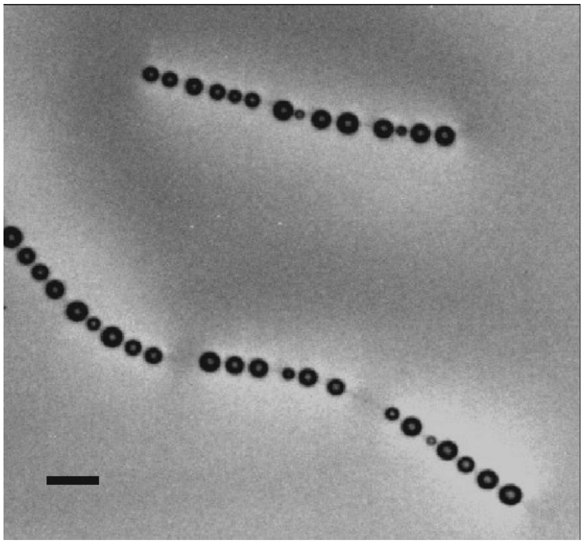

FIG. 4. Microscope picture of long droplets chains (black bar: 20 μm).

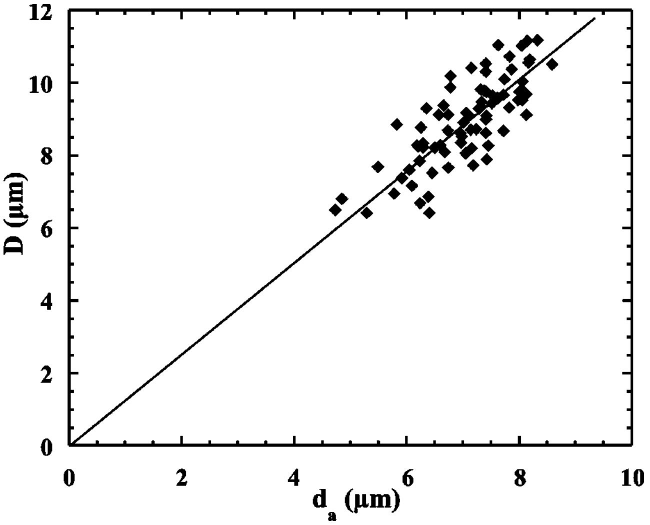

FIG. 5. Plot of the distance (D) between droplets center as a function of their average diameter (d_a), and linear fit.

In the present paper, we have studied the behavior of colloidal inclusions in 2D ordered films. The particles are accompanied by topological defects. The resulting particle-defect pairs allow far-field alignment of the **c** director. The in-plane elastic distortions induce dipolar elastic interactions, which cause the inclusions to form chains. These observations are closely reminiscent of the behavior of 3D nematics. However, thermal fluctuations of orientation and the occasional rotation of the particle-defect dipoles are distinctive features of 2D systems. The good agreement between theoretical predictions and the present experimental observations provides an important basis for the more general understanding of the behavior of colloidal inclusions in 2D films or membranes, such as Langmuir films or biological bilayers made of tilted phospholipids. Smectic films, in which elastic properties, film thickness, and size of inclusions, could be easily varied, may serve in the future as models to various systems independently of more complicated contributions usually found in surfactants or biological systems.

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