

Two-dimensional ordering of inclusions in smectic-C films

*P. Cluzeau, G. Joly, H. T. Nguyen⁺, V. K. Dolganov**

*Laboratoire de Dynamique et de Structure des Matériaux Moléculaires,
ESA CNRS 8024, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France*

⁺*Centre de Recherche Paul Pascal, CNRS, Université de Bordeaux I, F-33600 Pessac, France*

**Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow dist., Russia*

Submitted 3 April 2002

The organization of inclusions nucleated in free standing films of smectic-C (SmC) liquid crystal is investigated using polarized light microscopy. Anchoring on the inclusion boundaries induces distortions of the in-plane orientational order of the SmC phase which drive the elastic interactions between inclusions. Such interactions evidence a quadrupolar character. At low concentration, the inclusions self-organize in linear or branched chain structures while at high concentration two-dimensional patterns appear in the film.

PACS: 61.30.Jf, 82.70.Dd

Collective behaviour of dispersions of particles in a host fluid has been the subject of great interest over the past decade for science and technology [1–3]. In last years Liquid Crystals have become model objects for those investigations. The first reason is that in liquid crystals an effective interaction between the particles is realized via distortions of molecular ordering. The second reason is that the inclusions and resulting elastic deformation of the director field can be easily optically visualized with a polarizing microscope. In the field of Liquid Crystal emulsion (i.e. water or silicone oil droplets dispersed in a nematic host phase) the investigations put evidence of long range attraction and short-range repulsion between droplets that lead to formation of linear chains [1, 4–6].

Most of former investigations have been devoted to systems in which the director configuration around a particle is homeotropic, i.e. perpendicular anchoring of the molecules at particle surface. It was shown that if the particle is placed into a uniformly aligned director field a topological defect is created in the film in order to compensate the topological charge of the particle [7]. The particle and its associated defect form a topological dipole which drives long-range attraction between particles. Dipolar interactions between droplet-defect pairs lead to the formation of linear chains of droplets separated by point topological defects. Such chains were first observed in nematic (N) liquid crystal emulsion [1, 4–6] and recently in two-dimensional chiral smectic (SmC*) free-standing films [8, 9]. In nematic the preferred direction of the alignment of the molecules is specified by the unit vector field \mathbf{n} called the director. In smectic-C (SmC) phase, each layer is a two-

dimensional anisotropic liquid with rod-like molecules tilted in a given direction, the in-plane orientational order of the molecules in the smectic layers is specified by the so-called \mathbf{c} -director (projection of the average direction of the long molecular axis onto the layer plane).

In this paper we present investigation of particles in non-chiral smectic films with another type of inter-particle interaction. These particles exhibit planar anchoring of the \mathbf{c} -director, i.e. parallel to the particle's surface. We observed the formation of both linear structures and two-dimensional periodic lattice. Liquid crystal studied in our experiments is decyl oxybenzoic acid (DOBA), which exhibits the following phase sequence: Crystal – SmC – N – I [10]. We used material slightly doped with ethyl decyl oxybenzoate both to decrease the temperature of nucleation of the inclusions and to increase the temperature range of stability of the inclusions in the films. In a bulk sample of this mixture, the SmC-N phase transition ranges from 114 °C to 117 °C. In thick free standing films the nucleation of inclusions begins just above 114 °C. Free-standing films were prepared by drawing a small amount of the liquid crystal in the SmC phase across a 4 mm hole in a glass plate. The experiments were carried out on films with thickness from 1 to 3 μm . The temperature was controlled to within ± 10 mK. Microscopical observations are performed in reflected light between crossed polarizers, the texture varies from dark to bright according to the position of the \mathbf{c} -director with respect to the polarizers. A video camera enables dynamical observations. The determination of the film thickness and the direction of \mathbf{c} -director field is obtained from the reflection spectrum measurements.

Fig.1. Microscope picture of a single inclusion in the SmC free-standing film observed under crossed polarizers (horizontal and vertical). (a) and (b) figures correspond to the \mathbf{c} -director, respectively, at 45° and parallel to the polarization of the incident light. $T = 114.2^\circ\text{C}$. The horizontal size of each image is about $130\ \mu\text{m}$

Figure 1 presents the pictures of the droplets between crossed polarizers. Observations for two orientations of the film (the \mathbf{c} -director at 45° (Fig.1a) and parallel (Fig.1b) to the polarization of incident light) furnish more information about the distribution of the \mathbf{c} -director field deformation near the droplets. In dark regions in Fig.1a and in bright ones in Fig.1b the \mathbf{c} -director is rotated of about 45° with respect to its direction at long distances from the inclusion. Careful observation of Fig.1b reveals that the deformation of the \mathbf{c} -director field around the inclusion is not equivalent along vertical and horizontal direction. Two peculiarities are attached on left and right sides of the droplet boundary. Note that the orientation of the symmetry axis connecting these antipodal points is parallel to the \mathbf{c} -director field in the film.

The analysis of the process of nucleation and growth of droplets showed that the boundary of droplet is a defect line with tangential boundary condition. Droplets

nucleate inside a short double line and two parts of the defect line become the droplet boundary forming a loop. Director configuration around particle is homogeneous. There is only a breaking in the direction of tangential anchoring at the opposite points on the droplet boundary in which the ends of two line defects surrounding the droplet are connected. Dependence of surface droplet energy, defect line tension and elastic energy on inclusion dimension lead to the change of the droplet form. Small droplets (less than $15\ \mu\text{m}$) can have slightly elliptical form with the long axis oriented along the \mathbf{c} -director. Large droplets (above $15\ \mu\text{m}$) are nearly ideally circular (Fig.1b). It is worth mentioning that the droplet in Fig.1a has also a circular form. But it appears elliptical because the darkened regions occupy areas inside the droplet as well as outside. Circular inclusions may be conceived as oblate spheroids with a short axis a bit larger than the film thickness. The deformation of the film at the place of the inclusion is visible by observing the interference fringes in monochromatic light. Concerning the nature of the inclusions, both the temperature of nucleation, and the spheroid shape of the inclusions strongly suggest that the local order in the inclusion is nematic. In the case of smectic order in the inclusion, we should obtain a circular island of greater thickness than the background film [9]. Such an island exhibits a flat surface instead of a spheroid shape. The stability of the film is ensured by smectic layers surrounding the inclusion. Indeed, the air-liquid crystal interface is known to promote the smectic order.

Figure 2a schematically describes the director field around the droplet with planar anchoring on particle surface. The distortion near the peculiar points (M and N) is drawn in Fig.2b. The distribution of the director field near these points corresponds to a topological defect with strength equal to $1/2$. Note that the symmetry of \mathbf{c} -director in SmC phase does not permit isolated $1/2$ defect in the bulk of liquid crystal. However, such defects can exist when attached to a surface, in our case the inclusion boundary. The presence of a pair of singularities on the particle boundary preserve the zero topological charge of the film.

Zones with small distortion of the director field near each droplet are well visible in Fig.1b: (i) two acute zones starting from the opposite point defects; (ii) two larger zones in the orthogonal direction. As mentioned above, strong distortion of the \mathbf{c} -director field is mostly located in dark regions of Fig.1a and in bright regions of Fig.1b. These directions are expected to be the directions of attraction between neighboring inclusions. Spatial ordering of inclusions at equilibrium distance should minimize the \mathbf{c} -director deformation with respect to two

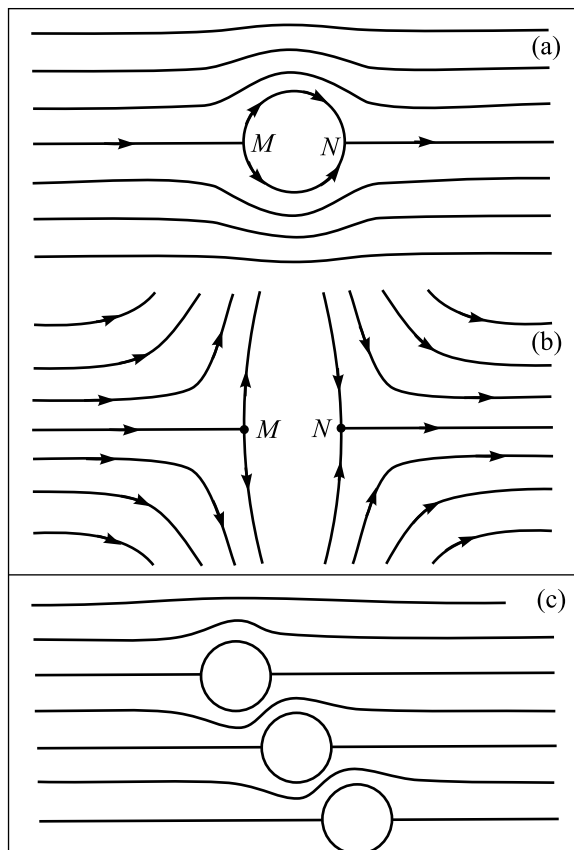


Fig.2. Schematic representation of the distortion of director field induced by inclusions. (a) and (b) figures correspond to the *c*-director configuration, respectively, near the single inclusion and near point disclinations. Two surface defects (*M* and *N*) are induced on the surface of the inclusion. *c*-director field configuration induced by a chain of inclusions (c)

isolated inclusions. Indeed, if several particles have nucleated they form chains as a rule (Fig.3). Formation of chains from spherical particles with planar anchoring was already observed in inverted emulsion (water droplets suspended in nematic liquid crystals) [4]. However, in chains, water droplets come into contact with one another that leads quickly to the droplet coalescence. In smectic films chains can be stable for a long time. Distortion of the director field is easily observed near the chains (Fig.3). The schematic drawing of the director field is given in Fig.2c. The chains form an angle of about 40° with respect to the *c*-director. Between the inclusions the *c*-director field has approximately the same direction coinciding with the direction of planar anchoring on the inclusion boundary. Such organization of inclusions minimizes the deformation of the director field in the film.

Fig.3. Microscope picture of a chain of four inclusions. Polarization of the incident light is along the horizontal axis. $T = 115.5^\circ\text{C}$. The horizontal size of each picture is about $130\ \mu\text{m}$

Interaction between particles with planar anchoring is of quadrupolar type [11]. This type of interaction leads to a higher possibility of structural organization than dipolar one. In this latter case, the attraction is maximal along the axis of the topological dipole i.e. along the *c*-director orientation at long distance [1, 8, 9]. Formation of linear chains is then a consequence of dipolar symmetry. The positions of two particles on both sides of a third one (central) are equivalent if the particles are located along a straight line. In the case of quadrupolar interaction there are two directions, and respectively four positions of particles, along which neighbouring particles may be located. Fig.4a shows bended chains. They appear when one of the particles is located in a nonequivalent position. Fig.4b shows two adjoined chains. The distances between particles in a chain and between the chains are practically identical. At high droplets density, a two-dimensional spatial oriented structure is built (Fig.5a, inclusions have slightly oblong shape). Such a degree of organization can only be achieved if all the particles exhibit approximately the same size. Those structures exhibit spatial ordering of the *c*-director configuration in the film

Fig.4. Microscope picture, between crossed polarizers, of complex structures formed by inclusions. Due to the quadrupolar character of the interactions the particles can have different positions with respect to the next neighboring particle. $T = 116.1^\circ\text{C}$. The horizontal size is about $130\ \mu\text{m}$

and orientational ordering of inclusions: lines connecting singular points on the inclusion boundary are oriented in a specific direction (the vertical direction in Fig.5a). A part of the film with two-dimensional ordering of circular particles is shown in Fig.5b. Generally, the nucleation of large particles leads to a distribution of the particle size which prevents the formation of large scale well-organized structure. The different orientations of the \mathbf{c} -director field between droplets are clearly visualized upon observation between crossed polarizers (Fig.5). Schematic representation of the director field between the particles is given in Fig.5c. Regions with nearly parallel orientation of the \mathbf{c} -director are located between nearest particles (dark regions in Fig.5a) and on the diagonals (dark regions in Fig.5b). However, these regions have different orientations of \mathbf{c} -director. That means that the \mathbf{c} -director does not keep the average di-

Fig.5. Two-dimensional ordering structure formed by inclusions (a). The structure is formed by slightly oblong inclusions. The square gives the unit pattern of the structure. The horizontal size is about $90\ \mu\text{m}$. (b) Part of the two-dimensional structure formed by circular inclusions. $T = 116.6^\circ\text{C}$. The horizontal size is about $50\ \mu\text{m}$. The polarizer is at 45° with respect to the horizontal axis (a) and along the horizontal axis (b). Schematic representation of the \mathbf{c} -director field for a two-dimensional structure (c)

rection over the whole area of the film. The presence of neighboring inclusions disturbs the pair interactions. As a consequence, binary interaction between inclusions usually used for modeling is insufficient to describe two-dimensional spatial and orientational ordering of inclusions.

In the present paper we have studied the behavior of nematic inclusions nucleated at the SmC-N transition in 2-dimensional ordered free standing films. After the nucleation process, spatially inhomogeneous inclusion distribution is achieved due to both long range attractive and short range repulsive interactions between particles. Such interactions result from the elastic deformation of the \mathbf{c} -director field induced by the tangential \mathbf{c} -director anchoring at the inclusions boundary. It should be noted that in the theoretical work [7], simulations about radial and tangential anchoring are treated and both lead to a -1 hyperbolic point defect associ-

ated with the inclusion. As a result, the inclusion – defect pairs always exhibit the dipolar symmetry and the radial and tangential anchoring only differ by the orientation of the topological dipole respectively parallel or normal to the \mathbf{c} -director field far from the inclusion. In our experiments, we observed two $1/2$ defects attached to the surface of the inclusion. The structural organization evidences a quadrupolar interaction which drives the formation of more complex structures than in the dipolar case. According to the inclusions densities different types of structure can be achieved: at low inclusions density linear and bend chains are built while at high density we observe 2-dimensional pattern resulting from positional and orientational ordering of the inclusions. This study underlines the role of the anchoring conditions at the inclusion boundary on the type of interaction. The dynamics of the self-organization and a model of interactions between inclusions are under investigation. The confrontation of the quadrupolar and dipolar interaction in free standing films provides an important basis for the more general understanding of the behavior of colloidal inclusions in membranes and 2-dimensional films, such as Langmuir films or biological phospholipid bilayers.

We are pleased to thank L. Lejcek and P. Poulin for helpful discussion. V.D. would like to thank the University of Lille I and Laboratoire de Dynamique et Structure des Matériaux Moléculaires for hospi-

tality. The work in Russia was supported by RFFI # 01-02-16507 (V.D.).

1. P. Poulin, H. Stark, T. S. Lubensky, and D. A. Weitz, *Science* **275**, 1770 (1997).
2. A. P. Ruhwandl and E. M. Zukoski, *Adv. Colloid Interface Sci.* **30**, 153 (1989).
3. W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge, 1989.
4. P. Poulin and D. Weitz, *Phys. Rev.* **E57**, 626 (1998).
5. T. C. Lubenski, D. Pettey, and N. Currier, *Phys. Rev.* **E57**, 610 (1998).
6. J.-Ch. Loudet, P. Barois, and P. Poulin, *Nature* **407**, 611 (2000).
7. D. Pettey, T. C. Lubensky, and D. R. Link, *Liquid Crystals* **25**, 579 (1998).
8. P. Cluzeau, P. Poulin, G. Joly, and H. T. Nguyen, *Phys. Rev.* **E63**, 031702 (2001).
9. P. Cluzeau, V. Dolganov, P. Poulin et al., *Mol. Cryst. and Liq. Cryst.* **364**, 381 (2001).
10. D. Demus, *Flüssige Kristalle in Tabellen*, VEB Deutscher für Grundstoff industrie, Leipzig, 1974; M. Petrov, A. Braslou, A. M. Levelut, and G. Durand, *J. Phys. France* **2**, 1159 (1992).
11. S. Ramaswamy, R. Nityananda, V. A. Raghunathan, and J. Prost, *Mol. Cryst. Liq. Cryst. Sci. Technol.* **A288**, 175 (1996).