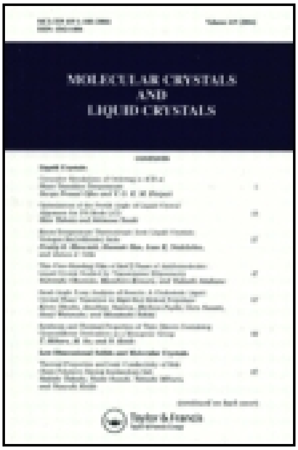

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Two-Dimensional Liquid Crystal Dispersions in Free Standing Films of Tilted Smectics

R. Najjar [a] & Y. Galerne [a]

[a] IPCMS/GMO, 23 rue du Loess BP-20, 67037, Strasbourg, France

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 475-485
Reprints available directly from the publisher
Photocopying permitted by license only

Two-Dimensional Liquid Crystal Dispersions in Free Standing Films of Tilted Smectics

R. NAJJAR and Y. GALERNE

IPCMS / GMO, 23 rue du Loess, BP-20, 67037 Strasbourg – France

We report on the appearance of small isotropic droplets or bubbles, in free standing films of a non-chiral symmetric mixture of MHTAC, which exhibits a SmC_A to isotropic phase transition. The isotropic droplets are initiated by applying a dc electric field tangentially to the film plane. Then, when increasing temperature towards the isotropic phase transition, the droplets are observed to grow. They then organize to form chainlike and Y-shaped structures. The formation of these structures evidences the existence of anisotropic interactions of the dipolar type between the droplets, with a long range attraction and a short range repulsion. The short range repulsion is reduced when the droplets become large, so that they eventually collapse with one another before being swallowed by the meniscus. Hence, the appearance of such droplets may also be viewed as a precursor mark of a thinning process of the free standing film.

Keywords: smectic C_A; colloidal dispersion; isotropic droplets; bubbles

I. INTRODUCTION

Recently, P. Poulin et al [1] observed interesting dispersions of water droplets in nematic liquid crystals, exhibiting short range repulsive and long range attractive interactions that originate from the elasticity of the surrounding nematic medium. It results that the observed dispersions are stable and that the droplets align in straight chains, parallel to the general direction of the nematic director **n**.

Here, we report on the observation of a dispersion of droplets of isotropic liquid crystal in a freely suspended smectic film of tilted smectic liquid crystal, which may be considered as similar in two dimensions, to the Poulin's experiment. The isotropic droplets are observed close to the isotropic phase transition, after the film has been intensively submitted to the hydrodynamic flows produced by a dc electric field. They correspond to the melting of one or a few smectic layers in the middle of the film. In this manner, the melted domains are flat and may be considered as 2D droplets. They eventually attract one another and form chainlike structures oriented in the **c** field of the suspended film of the tilted smectic.

II. EXPERIMENTAL

The sample is a freely suspended film of a symmetric mixture of MHTAC enantiomers (1-(methyl)-heptyl-terephtalidene-bis-amino-cinnamate) [2] [3]. The bulk phase diagram of MHTAC is:

$$\text{Crystal} \leftarrow 112°\text{C} \rightarrow \text{SmC}_A \leftarrow 158°\text{C} \rightarrow \text{isotropic.}$$

This compound is non-chiral and exhibits a smectic C_A phase (SmC_A). The SmC_A phase is a lamellar phase that resembles very much the SmC one (Fig. 1). The difference between them is that the molecular tilt occurs in alternate directions from one layer to the next one, which leads to a herringbone structure, in the SmC_A phase [4] [5].

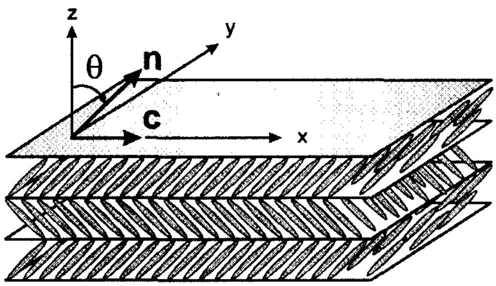

FIGURE 1. Herringbone structure of the SmC_A phase with the molecules tilted in alternate directions. The smectic layers are perpendicular to the z-axis.

Our experiments are performed on SmC_A films freely suspended on a square hole of a few millimeter size. The square hole is realized by means of two movable holders between two fixed ones (Fig. 2). Well controlled films of homogenous thickness are drawn in the SmC_A phase by putting the movable holders in contact to each other, spreading some amount of the liquid crystal substance on their edges, and carefully driving the holders apart. The film width is given by the distance between the fixed holders, which is about 5mm, while the film length can be varied from 0 to 7mm. The film and its frame are placed inside a thermally isolated hot stage, the temperature of which is regulated by means of a microcomputer. In this manner, the temperature of the sample may be controlled to up to ~ 0.01°C inside the temperature range of existence of the SmC_A (112°C - 158°C).

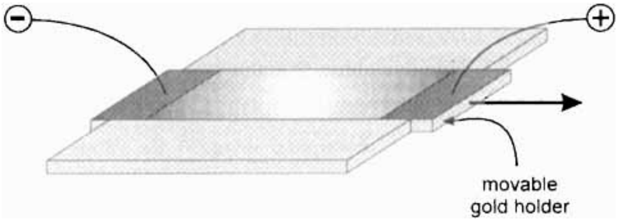

FIGURE 2: Sketch of a SmC_A free standing film. The movable holders are supplied with sputtered golden electrodes allowing the application of an electric field, which couples the **c** director to orient the film.

A dc electric field **E** can be applied tangentially to the film using gold electrodes sputtered on the two movable holders of the film frame. In this way, the film may be oriented uniformly, with the **c** director parallel to **E**, **c** being the unit vector along the projection of director **n** onto the smectic plane. The sample is observed in transmitted light between crossed polarizers with an Orthoplan (Leica) microscope carefully compensated from parasitic birefringence and able to resolve optical path differences between ordinary and extraordinary beams smaller than 0.5nm. The microscope is equipped with a Cohu video camera, which is connected to a 486 microcomputer via an IP8 (Matrox) video card.

III. ISOTROPIC DROPLETS FORMATION

When observed between crossed polarizers, the SmC_A free standing film exhibits textures in the dark grey scales, directly connected to the **c** distortions in the film. The dark grey color of the textures indicates that the thickness of the film is less than a few tens of layers. Consequently to an applied electric voltage ~ 100V onto the film, close to the isotropic phase transition, we may produce a lot of small circular domains all over the film (Fig. 3).

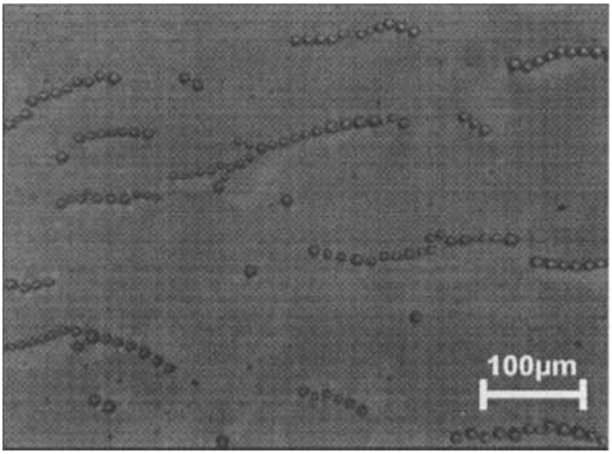

FIGURE 3. Photograph of chainlike structures of isotropic droplets observed in a SmC_A free standing film with even number of smectic layers, in the vicinity of the isotropic phase transition. Neighboring droplets are not in contact.

During the application of the electric field, a strong hydrodynamic flow appears due to the electric coupling to residual charges in the film [6]. The circular domains are darker than the rest of the film. This indicates that they are places where the film is optically thinner, and suggests that they correspond to isotropic domains, one or a few smectic layers thick. In this view, they are non-spherical but disklike droplets (Fig. 4). We may moreover argue that they are located inside the SmC_A film, close to its central part, if we remember the observation in the induced films, that the smectic layers are stabilized by the free surfaces, and conversely that they melt at the lowest temperature, the farthest they are from the air [5].

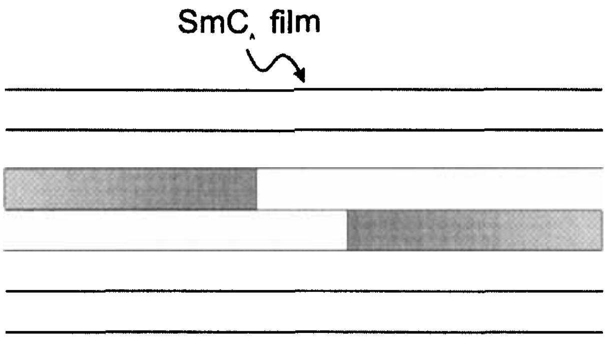

FIGURE 4. Sketch of the SmC$_A$ film with the isotropic domains located in two different single layers in the central part of the film. The isotropic domains are not spherical but disklike.

IV. TIME BEHAVIOR OF ISOTROPIC DROPLETS AND CHAIN FORMATION

At the beginning of their formation, the isotropic domains are small. Due to the finite resolution of the microscope, the isotropic domains appear as single points dispersed at random within the whole film. Their diameter is then less than ~ 1μm, and slowly increases with time. In order to increase their size faster, we slightly raise the temperature of the sample. An increase in temperature of a few degrees results in a significant increase of the size of the isotropic domains. They reach ~ 10μm in diameter and then keep constant if the temperature is stabilized. They exhibit a circular shape (Fig. 3) due to the tension of the dislocation line which limits them [8]. In the first stage, they are dispersed at random across the whole film, well separated from one another. Typically, the distance separating two isolated droplets is a few hundred micrometers, which correspond to a tenth times the droplets diameter. Then, the system is left to move around freely and the droplets are observed to attract each other spontaneously, moving very slowly. It results in the formation of chainlike structures and complicated compact clusters. By contrast with the aggregates usually observed, these clusters have anisotropic shapes with elongated chains further forming Y-shaped structures. When the temperature is kept constant, these structures are stable over a range of time about 4h, which is sufficient to allow comfortable observations. This also means that the droplets are stabilized by both attractive and repulsive interactions. They thus appear to be the 2D equivalent of the 3D dispersions of water droplets in nematic host fluids [1]. It is also analogous to that Cluzeau observed in ferroelectric samples [7].

In the experiment performed by Poulin et al. [1], both the long range attractive interactions and the short range repulsive interactions arise from the **n** elastic distortion in the nematic matrix. Moreover, the repulsive interaction really exists only if the **n** anchoring is strongly perpendicular to the water surface, enough to maintain a hedgehog defect in between the droplets. The attractive interaction is then of the dipolar type, which explains well the formation of chains and of Y-shaped structures. In our 2D system, the nematic director **n** is replaces by the director **c**, but the physics remains essentially the same, with **c** distortions producing the attractive and repulsive interactions between the droplets. Naturally, quantitative differences exist between the two systems. The two dimensional nature of the problem, the larger anisotropy of the elasticity in the tilted smectics, and the relatively weak anchoring of **c** onto the edge-dislocations measured in the induced films [8], probably explain that the distance which separates two neighboring droplets in a chain is twice larger than in 3D dispersions, i.e. ~ 1.3 times the droplet radius. Let us also notice that though the optical contrast is weak, the texture around an isolated droplet is observed to be asymmetric, consistent with a dipolar symmetry for the **c** director field. One may then ask why we do not observe hedgehog defects in the vicinity of the droplets. Apart from the limited resolution of our video-frames, the hedgehog defects are perhaps very close to the isotropic droplets, because of the weak anchoring of the **c** director onto the edge-dislocations [8]. The effect of a weak anchoring, when compared to a strong one, is to translate the **c** field lines closer to the anchoring surface by an amount of an extrapolation length ξ_0. In these conditions, the hedgehogs defects should be closer to the isotropic droplets than in the anchoring case, and therefore difficult to observe (Fig. 4). In a previous study, the anchoring of **c** onto edge-dislocations of different Burgers vectors in induced SmC_A films, has been shown to be normal in the case of simple dislocations with an extrapolation length $\xi_0 \sim 10\mu m$ [5]. Such an anchoring is consistent with our observation of a stable dispersion of droplets with dipolar attraction, and therefore suggests that our isotropic droplets are only one smectic layer thick. However, in our case, ξ_0 may probably be much larger than in induced SmC_A films, because of the symmetry of the free standing film.

When the diameter of the droplets increases and exceeds some critical value $\sim 50\mu m$, the droplets become unstable and eventually collapse with one another. At that moment the short range repulsion between the droplets has become weak or disappeared, probably because the hedgehog defects have been swallowed inside the growing droplets.

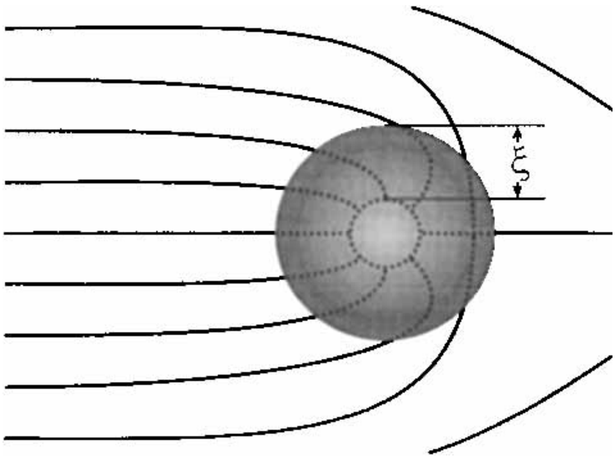

FIGURE 4: Schematic representation of the director field around an isotropic droplet. The limit of a strong anchoring condition at the surface of the droplet is represented by dashed lines. The weak anchoring condition limit is depicted with solid lines. If the extrapolation length ξ_0 is large, the hedgehog defect should be closer to the surface of the droplet.

V. TEMPERATURE BEHAVIOR OF THE ISOTROPIC DROPLETS

On increasing temperature closer to the isotropic phase transition, we observe that the size of the droplets increases. The same behavior is also observed on just waiting at a stable temperature that the chemical degradation has decreased the transition temperature and consequently, reduced the temperature distance to it. This second process is however very slow.

On further increasing temperature, when the isotropic droplets have become large, they eventually collapse until they are swept away by an edge-disclination line from the free standing film and drained off towards the meniscus. The parity of the film remains the same. Though the droplets, taken individually, are constrained in a single layer, they are probably dispersed in two separate layers. Then, the system comes back to a usual free standing film without any isotropic droplet, and exhibits a uniform texture. The sweeping away of the droplets may somehow be considered as the 2D equivalent of the phase separation, which occurs in classical emulsions when the short range repulsion is suppressed. During the sweeping process the film has got thinner because all the isotropic droplets have been evacuated into the meniscus by an edge-dislocation line, working as a piston. Thus, the formation of the droplets may also be viewed as a precursor mark of a thinning of the free standing film.

VI. CONCLUSIONS

The observations reported in this paper evidence a 2D colloidal dispersion of isotropic droplets inside a free standing film of tilted smectic. The isotropic droplets correspond to the melting of one or a few smectic layers located in the central region of the film. They do not form spontaneously. They are initiated by the application of a sufficiently large dc electric field, which induces strong irregular electroconvective flows in the free standing film. As in the 3D nematic dispersions, the interactions between the isotropic droplets arise from the orientational elasticity in the surrounding liquid crystal. They similarly lead to the formation of chainlike and Y-shaped structures. The repulsive short range interactions between the droplets are generally sufficient to prevent them to collapse, and the isotropic phase to separate from the rest of the SmC_A film. Nevertheless, this is what happens when the size of the droplets gets beyond a critical value above which the short range repulsion disappears leading to a progressive collapse of the isotropic droplets. Finally, the phase separation occurs while all the isotropic droplets are swept away from the film towards the isotropic meniscus.

Acknowledgments

The authors thank C. Germain and L. Oswald for synthesizing and crystallizing the LC compounds that we have used.

References

[1] Ph. Poulin, H. Stark, T.C. Lubensky, D.A. Weitz, *Science*, **275**, 1770, 1997; Ph. Poulin and D.A. Weitz, *Phys. Rev. E*, **57**, 626 (1998).
[2] The MHTAC molecule has two chiral centers. The compound used here is a symmetric mixture in the proportions: 25%++, 25%--, 50%+-.
[3] P. Keller, L. Liébert, and L. Strzelecky, *J. Physique Colloq.* **37**, C3 (1976).
[4] A. -M. Levelut, C. Germain, P. Keller, L. Liébert, and J. Billard, *J. Phys.* (Paris) **44**, 623 (1983).
[5] Y. Galerne, and L. Liébert, *Phys. Rev. Lett.* **64**, 906 (1990); Y. Galerne and L. Liébert, *Phys. Rev. Lett.* **66**, 2891 (1991).
[6] C. Langer and R. Stannarius, *Phys. Rev. E*, **58**, 650 (1998).
[7] Ph. Cluzeau, 9ème Colloque d'expression française sur les cristaux liquides, Tunisia (1999).
[8] V. Candel and Y. Galerne, *Phys. Rev. Lett.* **70**, 4083 (1993).