

Formation of two-dimensional crystal-like structures from inclusions in smectic C films

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Submitted 18 July 2002

The structures formed by inclusions in smectic C (SmC) free-standing films are investigated using polarized light microscopy. The domains confined in these two-dimensional (2D) systems induce distortion of the in-plane orientational order which governs the elastic interaction between the inclusions. The balance between long range quadrupolar attraction and short range repulsion gives rise to a non-trivial collective behaviour of domains. Various 2D structures are created as a function of the concentration and size of the inclusions. We observe the formation of chains and then 2D square lattice when the concentration of domains increases. Further increase of the domain size leads to the transition from square to hexagonal close packed structure.

PACS: 61.30.-v, 82.70.Dd

The study of dispersions of foreign particles in a liquid crystal host phase has attracted considerable interest in recent years [1–6]. Most of the investigations were performed in nematic (N) liquid crystals in which the molecules exhibit only an orientational order. The average direction of the long molecular axis is specified by the unit vector field \mathbf{n} called the director. The orientational elasticity of the nematic host phase gives rise to long range interaction between the particles. At long distances with respect to the inclusions size this interaction can be expanded in multipoles. Recent theoretical and experimental studies [1–7] have shown that the effective pair interaction exhibits dipolar or quadrupolar character depending on the boundary condition around the inclusion. In both cases attraction between inclusions induces the formation of chain structures. More recently interaction between inclusions was evidenced in smectic C (SmC) free-standing films [8, 9]. Such films appear as two-dimensional systems convenient for the investigation of the collective behavior of inclusions. Those films consist of an integer number of molecular smectic layers oriented parallel to the free interface bounded by air. In the SmC phase, each layer is a two dimensional anisotropic liquid with the long molecular axis tilted in a preferential direction with respect to the layer normal. The projections of the mean direction of the long molecular axis onto the layer plane define the two-dimensional (2D) field $\mathbf{c}(x, y)$ of molecular ordering called \mathbf{c} -director. Long-range attraction between inclusions results from

in-plane elastic deformation of the \mathbf{c} -director near inclusions [10]. The first experiments have shown [8, 9] that in 2D films the inclusions organize themselves in long chains like in 3D nematic emulsion. Most of the investigations were carried out with spherical droplets in nematic or with circular inclusion at relatively low concentration of inclusions in smectic film. But it appears quickly that anisotropic particles at high concentration should give rise to other interesting structures. For instance, it was predicted that the formation of various cellular structures depends on the shape and the concentration of the inclusions [11, 12]. Recently two-dimensional structures formed by inclusions were observed in nematic host phase [13] and in SmC films [14].

The present paper deals with anisotropic inclusions nucleated in relatively thick film just below the SmC-N transition temperature. Both the concentration and the size of the inclusions can be modified over a wide range. This interesting feature allows to generate 2D structures built with the inclusions and to study the evolution of their organization versus the inclusion size. The periodicity of the structures is governed by the balance between the long-range attraction and the short-range repulsive interaction. If the distance between domains is of the order or larger than their size the pair quadrupolar interaction potential leads to a cellular structure with square lattice. A decrease of the domain-domain distance induces an overlap of the \mathbf{c} -director field distortions. In this case short-range repulsive interaction between do-

Fig.1. Image of small domains in reflected light under crossed polarizers. At low concentration the domains organize in chain structure. The horizontal dimension of image is about $195 \mu\text{m}$, $T_0 - T = 2.1^\circ\text{C}$

mains plays the dominant role in the formation of cellular structure and leads to the transition into a close packed structure exhibiting hexagonal symmetry.

Liquid crystal used in our experiments is decyl oxybenzoic acid (DOBA), which exhibits the following phase sequence: Crystal – SmC – N – Isotropic [15]. This material is slightly doped with ethyl decyl oxybenzoate. In a bulk sample of this mixture, the SmC-N phase transition ranges from 114°C to 117°C . Impurities favors the nucleation of domains in the SmC film. The temperature of the transition of the whole film in nematic (T_0) in this case occurs at 117°C . A weak decrease of T_0 is observed along the time. This decrease may result from a degradation of the material. The films are achieved by spreading the material in the SmC phase across a circular hole (4 mm diameter) in a thin glass plate. The sample temperature is controlled with accuracy of $\pm 20 \text{ mK}$. In our experiments we used films ranging from 4 to $10 \mu\text{m}$. Both the nucleation process and the organization of the domains are observed using polarized light reflection and transmission microscopy. The images are recorded using a CCD camera.

The inclusions consist of domains confined in the uniform background SmC free-standing films. The domains nucleate on heating approximately 3°C below the SmC – N transition temperature in the film. Fig.1 shows the first stage of organization of the domains. At low concentration they form chains. The domains exhibit a slightly elliptical shape. Note that a weak deformation of the smectic film is generally induced by the inclusion along the normal to the layer (\mathbf{z} direction). Such a deformation of the film is visible by observing the thickness interference fringes in monochromatic light.

Fig.2. Image of a square lattice of inclusions in the SmC free-standing film observed in transmission between crossed polarizers. Polarizer is oriented at 45° with respect to the horizontal axis. $T_0 - T = 1.3^\circ\text{C}$. The horizontal size of image is about $160 \mu\text{m}$

Interaction energy between inclusions can be expanded in multipoles [2] that include the dipolar and quadrupolar terms. Dipolar attraction between inclusions is anisotropic and maximum in one direction. Consequently, dipolar interaction would induce a chaining of the inclusions along only one direction. In the present case, we observed the chain formation in two directions with the angle of about 110° between them (Fig.1). The observed two orientations of chains are the signature of nondipolar interaction. Quadrupolar interaction should be repulsive for directions parallel and perpendicular to the \mathbf{c} -director and becomes attractive in the intermediate directions [16]. The way of organization of the chains in Fig.1 evidences that quadrupolar interaction is larger than the dipolar one. As a consequence the final structure should be mainly determined by the quadrupolar interaction.

Fig.2 shows the film with domains of larger size and with a higher concentration. The increase of both size and density of domains leads to a 2D structure with square lattice. The large size of the domains enables to distinguish line defects that seem to fill the domains. Such lines have early been observed in free standing film [17–19] and on the free surface of the smectic droplets [20–22]. These lines should correspond to narrow variations of the director orientation but we can not infer from our observations if these lines are connected with SmC order inside the domains or only at their surface (i.e. in the smectic layers surrounding the inclusion). Actually, the type of order inside the domains remains unclear to us.

Interaction between inclusions depends on orientation of the \mathbf{c} -director near their boundary. In the immediate vicinity from line defects forming domain bound-

ary strong director deformation takes place and we can not speak about anchoring condition for the \mathbf{c} -director on the boundary. However, the joined action of line defects determines the orientation of \mathbf{c} -director on a short distance from domain boundary (about a few micrometers). The strong \mathbf{c} -director deformations are confined in a region close to the boundary that can be called the coat of the inclusion [23]. Inside the coat the elastic theory is not valid. We should consider the orientation of the \mathbf{c} -director outside the coat instead of the anchoring condition on the inclusion boundary. The symmetry of the distortion visible in Fig.2 is source of quadrupolar interaction [16, 24].

The texture observed in Fig.2 is characterized by positional ordering of the domain centers and also orientational ordering of their long axes. Those long axes are all oriented in the same direction. It should be noted that the periodic structure can be only achieved when the domains exhibit approximately the same size and line defects in the domains are parallel to their long axis. A change of domain size induces a defect in the periodicity (Fig.2). So, the observed chains and square structure can be qualitatively explained by pair quadrupolar interaction.

The above described square lattice is observed only if the ratio between the domain-domain distance and the square lattice parameter is higher than about 0.3. The heating of the film leads to an increase of domain size and as a result an evolution of the structure. As the domains mobility is low the distances between them decrease. So, increasing of the domain size should be similar to an increase of pressure. At short distances the domains shape tends to become nearly circular. In such case, the square lattice becomes instable and a reorganization of the structure occurs. Domains change their positions and form close packed hexagonal structure (Fig.3). Different domains are separated by a coat with strong distortion of the director field. Elastic theory with binary deformation interaction does not fit to explain the domain ordering. However, it is clear that a repulsive interaction exist between the coats. In film with high domain density there are no free regions without domain structure. As a result the domains cannot move in order to increase the inter-domain space. Even if the domains are close compact, the boundary between domains do not disappear and we do not observe coalescence. So, the repulsive interaction resulting from the large distortion of the \mathbf{c} -director in the coat is high enough to allow the formation of close packed hexagonal structure.

Finally, further heating leads to a filling of the whole area of the film by the domains (Fig.4). During the

Fig.3. Hexagonal lattice formed by close compact domains, $T_0 - T = 0.3^\circ\text{C}$. The horizontal dimension of image is about $260\ \mu\text{m}$

Fig.4. 2D hexagonal structure formed by hexagonal-like domains near the temperature of the film transition to nematic phase, $T_0 - T = 0.1^\circ\text{C}$. Horizontal dimension of image is about $260\ \mu\text{m}$

growth of the domains their shape becomes hexagonal-like. The boundary between domains appears as thick strain lines. These walls of a few microns thick should include strong distortions of the \mathbf{c} -director orientation which insure the stability of the structure. This structure with compact hexagonal-like arrangement is achieved close to the temperature of the SmC-N transition. Such a film can also be considered as a 2D smectic foam.

So, in SmC film of DOBA we observed the organization of domains in three types of structure. At low concentration, domains form chains. At intermediate concentration two-dimensional lattice with square cell is formed. These structures result from pair quadrupolar interaction. The disappearance of the square structure occurs above some critical domain size. This structure is replaced by a regular hexagonal lattice in which the inclusion are close compact. Further increase of the do-

main size decreases the free area between domains and induce the change of their shape. Thus, the increase of the compactness of the structure lead to the filling of the whole SmC film by hexagonal-like domains.

The essential feature of this system is that the anchoring conditions at the boundary of the domains do not seem well-defined. Thus, the interdomain interaction is probably mainly governed by the coat of different molecular orientations near domain boundary. Such a situation is probably typical for inclusions with complicated shape and molecular orientation on the boundary.

This experimental study underlines the influence of both the breaking of the symmetry of the *c*-director field in the vicinity of the inclusion and the anisotropic shape of domain on the structural organization of the inclusions confined in a membrane. Previous experimental studies both in film and in 3D system have established that the boundary conditions determine the type of interactions and lead to different organizations of inclusions. The present results demonstrate that the 2D structural organization can also be varied by the change of density and inclusion size. A comparison of the average size of domains and film thickness in order to classify the successive observed structures is under investigation. We expect that similar selforganization should be observed in other systems.

The authors thank the region nord-pas-de-calais and FEDER for funding of the image set-up. V.D. would like to thank the University of Lille I and Laboratoire de Dynamique et Structure des Matériaux Moléculaires for hospitality. In Russia the work was supported by the RFFI # 01-02-16507 (V.D.).

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