

Dimer structures formed in smectic films by inclusions with parallel and antiparallel topological dipole moments

*P. V. Dolganov, E. I. Kats⁺, V. K. Dolganov, P. Cluzeau**

Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow district, Russia

⁺Laue-Langevin Institute, F-38042 Grenoble, France, and

L.D. Landau Institute for Theoretical Physics RAS, 117940 GSP-1, Moscow, Russia

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

Submitted 31 July 2009

Self-organization of cholesteric and nematic droplets in smectic free-standing films is investigated. Strong tangential anchoring at the droplet boundary leads to nucleation of a topological defect and formation of a topological dipole from the droplet and the defect. The interaction between droplets results in assembly of the droplets in dimers and line chains. Topological dipoles of the droplet-defect pairs can be oriented in dimers with polar (ferroelectric) and nonpolar (antiferroelectric) ordering. In this paper we found novel dimer structures formed by droplets with different handedness of the \mathbf{c} -director field near the droplets. Depending on the relative magnitude of the droplet dipoles the resulting structure may be dipolar or quadrupolar. Formation of antiferroelectric dimers is discussed on the basis of electromagnetic analogy.

PACS: 61.30.-v, 81.16.Dn

Inclusions in liquid crystal media are a novel class of self-organized systems [1–14]. At low concentration inclusions form line and branched chains or various clusters [1–6, 12, 13]. At high concentration of the inclusions periodic ordered superstructures may be formed [5–8, 10]. Their investigations are interesting from the fundamental point of view as a challenging model system in condensed matter physics. In the real-space and real-time experiments self-organization in the system of particles may be studied. Not of less interest self-assembly in liquid crystals is for technical applications as a perspective method of preparing different structures from micro- and nanoparticles, ordered suspensions and emulsions [15]. While the realness of applications is certain only when commercial products are made, physics of inclusions in liquid crystal media does not require proof of its importance for fundamental science.

In this paper we investigate interaction and self-organization of nematic and cholesteric droplets in thin free standing Smectic- C ($\text{Sm}C$) and ferroelectric Smectic- C^* ($\text{Sm}C^*$) [16–18] films. Droplets with strong anchoring on the interface between the droplet and the smectic film deform the two-dimensional (2D) field of orientational molecular ordering (so-called \mathbf{c} -director field [16–18]) which results in nucleation of the topological defects in the \mathbf{c} -director field near the droplet or on the droplet boundary. Droplets minimize the energy of the elastic deformation of the \mathbf{c} -director by forming dif-

ferent structures from droplets. On large distances the interaction between droplets may be expressed in topological multipoles. In this paper we consider the most frequent experimental case of dipolar droplets. Until recently, only one structure formed by two inclusions was found and investigated, namely structure with the same handedness of the \mathbf{c} -director near inclusions. In these inclusions the dipole moments of inclusion-defect pairs are parallel and directed perpendicular to the far-field \mathbf{c} -director. The formed chain structure is also dipolar. This structure and the corresponding energetic minimum were considered to be the only one existing for two dipolar inclusions. However, it is well known in the physics of condensed matter that electric dipoles may form both polar (ferroelectric) and nonpolar (antiferroelectric) ordering. The same situation can be also expected for topological dipoles. In this paper formation of structures in which the dipolar moments of the inclusions are completely or partially compensated, is observed. These structures are formed from inclusions with opposite handedness. In isolated inclusions the dipole moments are antiparallel. If the size of the particles and moduli of the dipolar moments are equal, a topological quadrupole is formed. Assembly of these structures means that the interparticle interaction at small distance is more complex than considered before and leads to formation of several energetical minima for the relative position of the particles.

Most experiments were carried out on free standing films of chiral *S*-4'-undecyloxybiphenyl-4-yl 4-(1-methylheptyloxy)benzoate (11BMSHOB) [19], racemic 11BMSHOB and their mixtures. The sequence of phase transitions in the bulk sample was $SmC^*-(108.2^\circ C)-N^*-(123.9^\circ C)-I$ in the chiral material and $SmC-(108.3^\circ C)-N-(124^\circ C)-I$ in the racemate. Some of the measurements were performed on chiral 9BSMHOB [19]. Films were prepared by spreading the liquid crystal in the smectic phase across a 4-mm circular hole in a glass plate. We used films with thickness from 8 to 40 smectic layers. The thickness of the film and the number of smectic layers N were determined from the optical reflectivity [17]. In thick films ($N > 20$) cholesteric or nematic droplets nucleate near the temperature T_c of the bulk transition from smectic to the high-temperature phase. In thinner films the droplets nucleate at higher temperatures slightly below the temperatures of the thinning transitions [20, 21]. The configuration of the *c*-director field near the droplets was observed with an optical microscope in the reflection mode. Observations were performed using depolarized reflected light microscopy (DRLM) [22] and polarized reflected light microscopy (PRLM). By a combination of these methods we can determine the configuration of the *c*-director field near the droplets. The images of the droplets and textures in the films were taken with a CCD camera.

We start with considering different types of single dipolar droplets that are formed in smectic films (Fig.1a,b,c). Droplets with a topological defect on the droplet boundary (Fig.1a) have topological charge $S = 0$. These droplets nucleate in the region of the film without topological defects. During the nucleation the topological charge of the film is conserved ($S = 0$). The orientation of the *c*-director on the droplet boundary is planar, i.e. the *c*-director is parallel to the droplet surface. Configuration of the *c*-director on the droplet surface and in the whole film may be obtained if we consider a virtual topological defect with charge $S = +2$ in the droplet center and the defect with charge $S = -2$ on the droplet surface. The topological dipole moment of the droplet with accompanying defect $d = \sum S_i r_i$ points from the defect to the droplet center and equals $d = 2R_0$, where R_0 is the radius of the droplet.

In presence of topological defects in the film prior to droplet nucleation, dipolar droplets of another type may be formed. On heating the droplet may nucleate in the center of a topological defect with charge $S = +1$ and attract the topological defect with charge $S = -1$ if such a defect exists in the film. They form a droplet-defect pair [23] in which the defect is in the film near the droplet (Fig.1b). The equilibrium distance from the

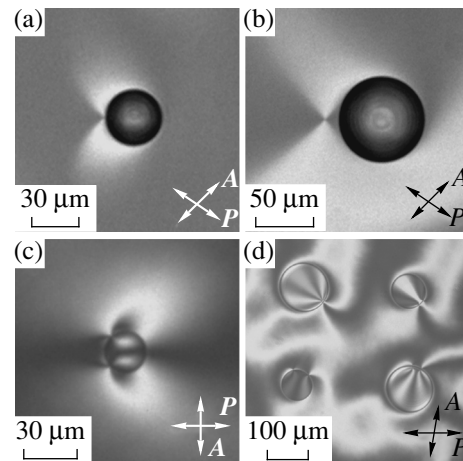


Fig.1. Cholesteric and nematic dipolar droplets and smectic islands in smectic films. (a) A droplet with an $S = -1$ defect on the droplet surface. (b) A droplet with accompanying $S = -1$ topological defect in a smectic film. (c) A droplet with two $S = -1/2$ surface defects. (d) Dipolar islands in a smectic film with different positions of the topological defects. (a), (b), (d) Ferroelectric 11BMSHOB films, (c) racemic 11BMSHOB mixture. DRLM (a), (b), (d), PRLM (c)

defect to the droplet center r_0 depends on the droplet radius: $r_0 = \sqrt{2}R_0$ [24]. According to the electromagnetic analogy [24] the *c*-director configuration in the film with a droplet-defect pair is equivalent to a configuration formed by an $S = +2$ defect in the droplet center and two $S = -1$ defects on the distance $\sqrt{2}R_0$ and $R_0/\sqrt{2}$ from the droplet center. The topological dipole moment of the droplet-defect pair $d = (3/\sqrt{2})R_0$ is somewhat larger than for a droplet with the defect on the droplet boundary.

A third type of the dipolar droplet with two $S = -1/2$ defects on the droplet boundary is shown in Fig.1c. In ferroelectric films such a droplet can be formed from a dipolar droplet (Fig.1a) by splitting the $S = -1$ defect in two $S = -1/2$ defects due to the competition between quadratic and linear elasticity [9, 11, 14, 25]. The defect angle α at which the two defects are seen from the droplet center may be changed by changing the temperature or droplet size [14]. The topological dipole moment of such droplets becomes $d = 2R_0 \cos \alpha/2$. According to theory [26, 27] in nonpolar films minimum energy corresponds to a quadrupolar droplet with two $S = -1/2$ surface defects on the opposite sides of the droplet ($\alpha = 180^\circ$). However droplets with $\alpha \neq 180^\circ$ (Fig.1c) can also be observed [8]. They may be formed from quadrupolar droplets. The reason leading in nonpolar films to the formation of dipolar

lar droplets with two surface defects is not known. The topological dipole moments for the droplets in Fig.1a,b,c point in the horizontal direction from left to right.

On cooling below T_c the droplets transform in smectic islands (Fig.1d) thicker than the surrounding film. Positions of the topological defects (Fig.1d) can be different as well as in the case of dipolar droplets. Hereafter we will discuss the formation of the dimers and chains from dipolar droplets.

At large droplet separation R they interact as $2D$ dipoles. The long-range interaction energy F_d is given by [24]

$$F_d = \pm \frac{2\pi K d_1 d_2}{R^2} \cos 2\varphi, \quad (1)$$

where d_1 and d_2 are topological dipole moments of droplet-defect pairs, K is the $2D$ orientational elastic constant, φ is the angle between the topological dipole of one of the droplets and the line connecting the two droplets. In Eq. (1) sign minus stands for parallel dipoles and plus for antiparallel ones. Following Ref. [28] we call the droplets with the line of droplet centers parallel and perpendicular to the topological dipole, respectively, longitudinal and lateral droplets.

Here we consider the structures formed by dipolar droplets. We start with droplets with the same handedness that is with parallel topological dipoles. At large distance longitudinal droplets attract each other. At small distance the attractive interaction changes to repulsion when the surface or bulk accompanying defect is approached to the surface of the other droplet with strong surface anchoring of the c -director. Dimers and line chains with a fixed distance between the droplets are formed (Fig.2a,b). These structures are dipolar with defects located between the droplets. The dipole moment is the sum of the dipole moment of individual droplets. Stable line structures are formed from droplets with surface (Fig.1a), bulk (Fig.1b) $S = -1$ defect and with two $S = -1/2$ surface defects (Fig.1c). The existence of an energetical minimum at a finite distance between droplets was obtained by numerical calculations only for the case of the bulk $S = -1$ defects [29, 30]. However the reason for droplet chaining may be understood from a qualitative consideration. Chains form due to the competition of attractive and repulsive interactions which natures are clear. Until nearest time only dipolar dimers and chains formed by droplets with parallel dipoles were observed in the case of dipolar inclusions.

In this work we demonstrate the existence of two other structures (Fig.2c and Fig.2d). These structures are formed from dipolar droplets with opposite c -director rotation around the droplets. In isolated

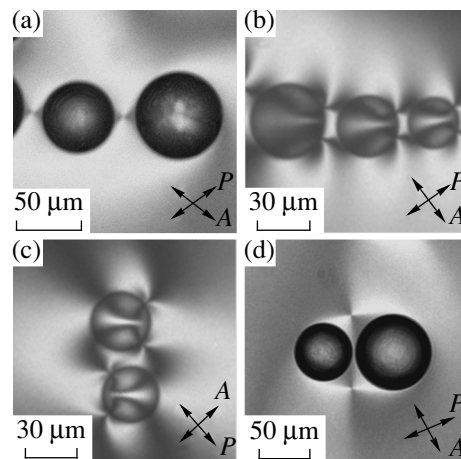


Fig.2. Dipolar droplets with parallel dipole moment self-organize in linear dipolar chains (a), (b). Dipolar droplets with antiparallel dipole moments can form dimers with $S = -1/2$ defects (c) and with two binding $S = -1$ defects (d). The images were taken using DRLM (a), (d) and PRLM (b), (c). Ferroelectric films (a,d), racemic mixture (b), (c)

droplets the directions of the topological dipole moments are opposite. We briefly review the reason of existing droplets with opposite direction of the dipole moments. In nonpolar films the droplets with different handedness that is with clockwise and counterclockwise director rotation around the droplets have equal energy and may nucleate with equal probability. In a polar film the linear over gradients of the order parameter term in the free energy favors one direction of the bend deformation near the circular inclusion. In a droplet with a surface defect the direction of the c -director rotation may change with temperature and droplet size [14], so that in some temperature range the droplets with opposite c -director rotation can exist [31]. Droplets with bulk defects and opposite dipole orientations may be formed from $S = -1$ defects and $S = +1$ droplets with opposite c -director rotation on the droplet boundary.

The quadrupolar dimer (Fig.2c) consists of two $S = +1$ droplets with surface $S = -1/2$ topological defects. The droplets have opposite directions of the topological dipole moments. In the upper droplet the dipolar moment is directed from right to left. In the lower droplet the dipole moment points from left to right. The orientation of the dimer depends on the angle α between $S = -1/2$ defects. At intermediate distances depending on the defect angle both dipolar and quadrupolar interaction with different angular dependence may be essential for these droplets. At small distance repulsive interaction arises since $S = -1/2$ defects approach the

other droplet. A dimer with an equilibrium distance between the droplets is formed. If the moduli of the dipolar moments of inclusions are equal, the dimer is quadrupolar with antiferroelectric ordering.

Another structure formed by the droplets with opposite handedness is the dimer in Fig.2d. This dimer consists of two $S = +1$ droplets and two bulk $S = -1$ topological defects. They form a symmetric structure with droplet line oriented perpendicular to the undistorted far-field \mathbf{c} -director. The orientation of the dimer is the same as for dipolar chains in Fig.2a,b. Both dimers can be formed from droplets with bulk defects. However the bonds between droplets differ essentially. For dipolar chains (Fig.2a) one $S = -1$ topological defect between droplets binds the droplets together. The second defect is on the opposite side of the droplets and practically does not influence on the bond between droplets. For the dimer in Fig.2d two $S = -1$ defects form bonds between the droplets. The defects are shared in an equivalent manner by each droplet. The distance between the droplets is smaller than for droplets with parallel dipoles. This situation closely resembles single and double covalent bonds in molecules. However the dimer with two binding $S = -1$ defects is a less stable structure. Closely spaced droplets (Fig.2d) within some time after forming of the dimer coalesce. Meanwhile dipolar dimers and chains (Fig.2a,b) exist for a long time. At least at a constant temperature we did not observe coalescence of these droplets. It may mean that the repulsive interaction between the droplets in the dimer with two binding $S = -1$ defects is weaker than in the dimer with a single binding $S = -1$ defect. If the size of the inclusions and the moduli of the dipole moments of the inclusions are equal, the dimer with two binding $S = -1$ defects is quadrupolar.

A qualitative explanation of the formation of dimer with two binding $S = -1$ defects (Fig.2d) on the base of the competition of long range and short range interparticle interactions is more complicated than the formation of dimers with a single binding defect. Dipolar (Fig.2a,b) dimers and chains are assembled in a natural way i.e. in the direction in which the droplets attract at long distance. This is not the case for the dimer in Fig.2d. The long axis of the dimer orients in the direction in which the droplets repel at large distance. This is why only very seldom such kind of counter-intuitive structures are observed in experiments. However, this repulsion holds only in asymptotic “far-field” range of inter-droplet separations. For smaller distances one can expect quite different (even in its sign) pairwise potential (especially for droplets with opposite chirality). There is also another peculiarity of this dimer. At for-

mation of the dimers and chains in Fig.2a,b the positions of the topological defects remain practically unchanged with respect to individual droplets. In the dimer in Fig.2d the topological defects changed their orientation with respect to the orientation in single droplets. Let us consider the change of the energy due to the azimuthal shift of the defects. Additional distortion of the \mathbf{c} -director is equivalent to the appearance of the “electric charge” $q = \phi / \ln(L/R_0)$ [24], where ϕ is the angle of the rotation of the defect with respect to the equilibrium azimuthal location, L is the size of the system. The energy associated with this distortion is similar to the energy of a circular inclusion with charge q [24]

$$F_q = \pi K q^2 \ln(L/R_0). \quad (2)$$

The interaction energy of two “charged” inclusion-defect pairs depends logarithmically on the droplet separation R [24]

$$F_{in} = -\pi K q_1 q_2 \ln(R^2/R_1 R_2), \quad (3)$$

where q_i and R_i are the “electric charges” and radii of the droplets. In our opinion at small distances the transformation of the interaction energies F_d , F_q , F_{in} can lead to the azimuthal shift of the defects and formation of the dimer with two binding $S = -1$ defects.

In summary, interaction of the inclusion-defect pairs on small distance is rather complicated and leads to the formation of dipolar and quadrupolar structures with different orientation with respect to the far-field director orientation. Droplets with parallel dipole moments form dipolar dimers and chains. Droplets with antiparallel dipolar moments may also form dimers. The dipole moment of these dimers depends on the difference between dipolar moments of the droplets. If the moduli of the droplet dipoles are equal, dimers formed by inclusions with opposite handedness become quadrupolar.

When the manuscript has been prepared for publication we learned that the quadrupolar dimer from smectic islands similar to the one we observed from droplets (Fig.2d) was found by Pattanaporkrattana et al. [32].

We thank A. Babeau and S. Gineste for synthesis of the liquid crystals.

-
1. P. Poulin, H. Stark, T. C. Lubensky, and D. A. Weitz, *Science* **275**, 1770 (1997).
 2. T. C. Lubensky, D. Petey, N. Currier, and H. Stark, *Phys. Rev. E* **57**, 610 (1998).
 3. J.-C. Loudet, P. Barois, and P. Poulin, *Nature (London)* **407**, 611 (2000).
 4. P. Cluzeau, P. Poulin, G. Joly, and H. T. Nguyen, *Phys. Rev. E* **63**, 031702 (2001).

5. V. G. Nazarenko, A. B. Nych, and B. I. Lev, *Phys. Rev. Lett.* **87**, 075504 (2001).
6. P. Cluzeau, G. Joly, H. T. Nguyen, and V. K. Dolganov, *Pis'ma v Zh. Eksp. Teor. Fiz.* **75**, 573 (2002) [*JETP Lett.* **75**, 482 (2002)]; P. Cluzeau, G. Joly, H. T. Nguyen, and V. K. Dolganov, *Pis'ma Zh. Eksp. Teor. Fiz.* **76**, 411 (2002) [*JETP Lett.* **76**, 351 (2002)].
7. P. V. Dolganov, E. I. Demikhov, B. M. Bolotin et al., *Eur. Phys. J. E* **12**, 593 (2003).
8. C. Völtz and R. Stannarius, *Phys. Rev. E* **70**, 061702 (2004).
9. P. V. Dolganov, H. T. Nguyen, G. Joly et al., *Europhys. Lett.* **76**, 250 (2006).
10. I. Mušević, M. Škavabot, U. Tkalec et al., *Science* **313**, 954 (2006).
11. C. Bohley and R. Stannarius, *Eur. Phys. J. E* **23**, 25 (2007).
12. P. V. Dolganov, H. T. Nguyen, E. I. Kats et al., *Phys. Rev. E* **75**, 031706 (2007).
13. C. Bohley and R. Stannarius, *Soft Matter* **4**, 683 (2008).
14. P. V. Dolganov and P. Cluzeau, *Phys. Rev. E* **78**, 021701 (2008).
15. W. Russel, D. Saville, and W. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge, U.K., 1989.
16. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed., Clarendon Press, Oxford, 1993.
17. P. Pieranski et al., *Physica A* **194** 364 (1993).
18. W. H. de Jeu, B. I. Ostrovskii, and A. N. Shalaginov, *Rev. Mod. Phys.* **75**, 181 (2003).
19. P. Cluzeau, M. Ismaili, A. Annakar et al., *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **362**, 185 (2001).
20. T. Stoebe, P. Mach, and C. C. Huang, *Phys. Rev. Lett.* **73**, 1384 (1994).
21. P. V. Dolganov, H. T. Nguyen, G. Joly et al., *Zh. Eksp. Teor. Fiz.* **132**, 756 (2007) [*JETP* **105**, 665 (2007)].
22. D. R. Link, G. Natale, R. Shao et al., *Science* **278**, 1924 (1997).
23. P. V. Dolganov, H. T. Nguyen, G. Joly et al., *Eur. Phys. J. E* **25**, 31 (2008).
24. D. Pettey, T. C. Lubensky, and D. R. Link, *Liq. Cryst.* **25**, 579 (1998).
25. J. Fukuda, *Eur. Phys. J. E* **24**, 91 (2007).
26. J. Fukuda and H. Yokoyama, *Eur. Phys. J. E* **4**, 389 (2001).
27. M. Tasinkevych, N. M. Silvestre, P. Patricio, and M. M. Telo da Gama, *Eur. Phys. J. E* **9**, 341 (2002).
28. C. Zhou, P. Yue, and J. J. Feng, *Langmuir* **24**, 3099 (2008).
29. P. Patricio, M. Tasinkevych, and M. M. Telo da Gama, *Eur. Phys. J. E* **7**, 117 (2002).
30. K. S. Korolev and D. R. Nelson, *Phys. Rev. E* **77**, 051702 (2008).
31. P. V. Dolganov, V. K. Dolganov, and P. Cluzeau, *Zh. Eksp. Teor. Fiz.* **136**, 197 (2009) [*JETP* **109**, 169 (2009)].
32. A. Pattanaporkrattana, C. S. Park, J. E. Maclennan et al., Submitted for publication; N. M. Silvestre, P. Patricio, M. M. Telo da Gama et al., Submitted for publication, arXiv:cond-mat.soft/0904/2713.