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# Joint scientific session of the Physical Sciences Division of the Russian Academy of Sciences and the Joint Physical Society of the Russian Federation "Liquid crystals" (28 February 2005)

A joint scientific session of the Physical Sciences Division of the Russian Academy of Sciences (RAS) and the Joint Physical Society of the Russian Federation "Liquid crystals" was held on 28 February 2005 in the conference hall of the P N Lebedev Physics Institute, RAS.

The following reports were presented at the session:

(1) **Dolganov V K** (Institute of Solid State Physics, RAS, Chernogolovka, Moscow region) "Structures and phase transitions in thin liquid-crystal films";

(2) **Palto S P** (A V Shubnikov Institute of Crystallography, RAS, Moscow) "Electrooptics and photonics of liquid crystals".

An abridged version of the reports is given below.

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## Structures and phase transitions in thin liquid-crystal films

V K Dolganov

### 1. Introduction

Liquid crystals have been a focus of research over the last decades by virtue of their interest for fundamental physics and as materials having a wide array of technological applications. The following areas of liquid crystal studies can be distinguished:

(1) The search and investigation of new types of liquid crystal structures. In spite of the more than 100-year history of liquid crystals, the number of molecular structures able to exist in the liquid crystalline state continues to grow; it is not infrequently that newly synthesized substances turn out to possess unusual structures having no analogs among previously obtained materials. A recent example is structures formed by banana-like molecules;

(2) Studies aimed at creating a new generation of information display systems with special reference to the use of polar liquid crystals and bistability effects;

(3) Studies of biological objects exhibiting elements of liquid crystalline ordering;

(4) Basic liquid crystal research.

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The majority of these studies are of general interest from the physical point of view. Examples include studies on the effects of the surface and the restricted sizes of a sample on its structure, phase transitions and physical properties, interactions, and self-organization of large particles (measuring microns or dozens of microns) in liquid crystal films, which are the subject of the present communication. A common feature of all these studies is the focus on thin liquid-crystal films.

Smectic liquid crystals have a layer structure with a layer thickness commensurate with the length of the organic molecules ($\sim 3$ nm) of which they are composed [1]. In the simplest smectic liquid crystal — that is, smectic $A$ (Sm $A$) — long molecular axes are perpendicular to the plane of smectic layers. In smectics $C$, molecules are tilted through an angle $\theta$ relative to the smectic layer normal. The large variety of smectic $C$ structures may be due to different azimuthal orientations of the molecules (angle $\varphi$) in their layers. In Sm $C$, all molecules are tilted in one direction, forming a synclinic structure. In the Sm $C^*$ ferroelectric phase, chirality of the constituent molecules is responsible for a structure twisted along the smectic layer normal. The Sm $C_A^*$ antiferroelectric phase is characterized by the molecules in the adjacent layers being tilted in opposite directions, giving rise to an anticlinic structure. The Sm $B$ structure possesses orientationally ordered bonds in the plane of the smectic layers.

Smectic liquid crystals can form freely suspended thin films varying in thickness from two to hundreds of molecular layers. Both surfaces of such films are in contact with the air, which makes them distinct from films deposited on a substrate, which tends to distort the structure of the surface layers. It is possible to produce high-quality films devoid of surface defects (steps, and the like), dislocations, and orientational defects. These properties make freely suspended films very convenient to study.

### 2. Effects of the surface and restricted sizes of liquid crystal films on the structure, phase transitions, and physical properties

There can be distinguished three surface effects:

(1) A purely geometric factor — that is, the surface layers interact with smectic layers only at one side of the surface;

(2) A surface makes up a physical interface between two media. Surface tension suppresses fluctuations of smectic layers near the surface, and their amplitude is much smaller than in the bulk. Specifically, the surface layers possess a higher degree of ordering (i.e., a higher value of the order

parameter) than the bulk ones. In films, these two effects may compete with each other;

(3) Effects of spatial restriction and interaction between the film surfaces, which acquire significance in thin films.

One of the most remarkable experimental effects in which the competition between the bulk and the surface properties of smectics shows itself is a layer by layer thinning of smectic films [2–5]. Thin smectic films do not melt at the phase transition temperature $T_C$ in a bulk sample. Instead, there occurs a series of transitions resulting in a decrease in film thickness by one layer. Thinning starts at a temperature somewhat higher than $T_C$ and ends when the film becomes as thick as two molecular layers. A two-layer film is destroyed (ruptured) at $T \approx T_C + 30$ K. During each thinning transition, matter from one molecular layer retreats toward the edge of the film (into the meniscus) and moves there in the molten state. The temperature dependence of thinning transitions is close to that of the correlation length of the smectic ordering that exists locally in a bulk sample above the melting point. The flat film surface stabilizes the smectic structure in the surface layer above the phase transition temperature in the bulk. When the correlation length $\xi_S$ of the surface ordering is sufficiently large, the layer ordering induced by the two surfaces is effectively overlapped, and the entire film is translationally ordered. A decrease in $\xi_S$ with temperature leads to a decrease in the translational order parameter at the center of the film and gives rise to structural instability. Stabilization of the translational ordering in the film is due to a decrease in its thickness (mediated through the nucleation and enlargement of the dislocation loop). By this means the melting temperature $T_C$ is substituted in a thin film by the structural instability temperature $T_N$ depending on the film's thickness. The number $N$ of film layers actually becomes a discrete free parameter, a change of which prevents melting and leaves the film translationally ordered.

Layer by layer thinning of smectic films clearly demonstrates the possibility of a substantial transformation of phase transitions in small samples. This example also shows how the surface can change. In the case being considered, the surface structure remains the same as in the bulk. The transformation of the phase transition is due to the difference between the order parameters at the surface and in the bulk of the film. In the high-temperature phase, a large sample contains regions of correlated molecular arrangement that are the precursors of a phase transition and are characterized by a correlation length. In films, temperature variations of the correlation length are directly manifested as a temperature-dependent change in the film thickness. Other effects can also be observed near $T_N$ due to the structural instability of the film, in particular, formation of a network of linear defects with a rupture of the two-dimensional field of the molecular orientational ordering [5].

Nonuniformity of the order parameter profile in thin films is responsible for their markedly altered physical characteristics compared with those in the bulk sample. An example is provided by the transformation of polar characteristics. In a ferroelectric Sm $C^*$ liquid crystal (polar group of symmetry $C_2$), volume polarization is directly related to the chirality of the molecules [6]. Chirality brings about the formation of a spiral structure and polarization $P_T$ perpendicular to the local plane of the molecular tilt (transverse polarization). Transverse flexoelectric polarization $P_T^f$ is proportional to $\partial\varphi/\partial z$. However, generally speaking, the appearance of polarization

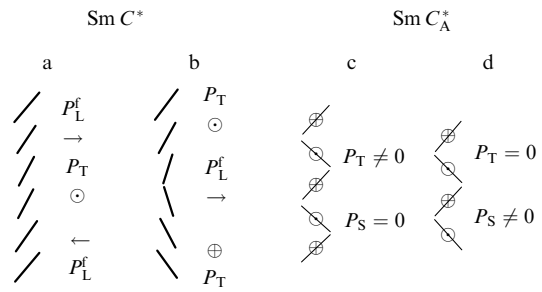


**Figure 1.** Orientation of long molecular axes in Sm $C^*$ films with transverse (normal to the plane of molecular tilt) $P_T$ (a) and longitudinal (parallel to the plane of molecular tilt) $P_L^f$ (b) electric polarization [7]. Smectic layers are arranged horizontally. Thin Sm $C_A^*$ films [8] with an odd and even number of molecular layers possess transverse $P_T$ (c) and longitudinal $P_S$ (d) polarizations, respectively.

is not necessarily associated with chirality (i.e., with a change in $\varphi$ or twist deformation). The orientational order in tilted smectic phases is characterized by a two-component order parameter $\psi = \theta \exp(\mathrm{i}\varphi)$. In the films, the order parameter modulus (tilt angle $\theta$ of the molecules) near the surface is higher than in the middle of the film (Fig. 1a). The resulting flexoelectric polarization $P_L^f$ is proportional to $\partial\theta/\partial z$ and lies in the plane of molecular tilt (longitudinal polarization) [7]. A change in the tilt angle of molecules in the adjacent layers (bending strain) may exceed deformation due to chirality. It is estimated that longitudinal polarization may be as large as $10^{-4}$ C m$^{-2}$; in other words, it is commensurable with or higher than transverse polarization at high temperatures. At low temperatures — that is, at a large tilt angle of molecules in the middle of the film, the latter possesses transverse polarization $P_T$ because longitudinal polarizations in its upper and lower parts have opposite directions and are mutually compensated (Fig. 1a). At high temperatures (above the temperature of an Sm $C^*$ – Sm $A$ bulk phase transition), the tilt angle $\theta$ of molecules at the center of the film is small. The film acquires a configuration at which molecules at its top and bottom are tilted in opposite directions (Fig. 1b). In such a structure, transverse polarizations $P_T$ in two halves of the film are counterbalanced, while longitudinal polarization $P_L^f$ in the entire film is directed to one side. This mechanism of induction of polarization is unrelated to chirality, so it is also realized in smectic films of nonchiral (Sm $C$) liquid crystals [7].

In the anticlinic structure of antiferroelectric liquid crystals (Sm $C_A^*$), adjacent layers undergo polarization in opposite directions; therefore, a bulk sample possesses no electric polarization. Thin films, unlike bulk samples, possess electric polarization [8]. The symmetry of thin films allows transverse polarization in those with an odd number of molecular layers, and longitudinal polarization in films with an even number of layers [8]. The two polarizations have different origins. In films with an odd number of layers, transverse layer polarization $P_T$ is uncompensated (see Fig. 1c: polarization of three layers is directed into the plane of the figure, and that of two layers out of it). Films with an even number of layers possess no transverse polarization because the number of layers in which molecules are tilted in one direction equals that where the tilt is in the opposite direction (Fig. 1d). The longitudinal polarization $P_S$ in these films is associated with the modification of surface layers. It is

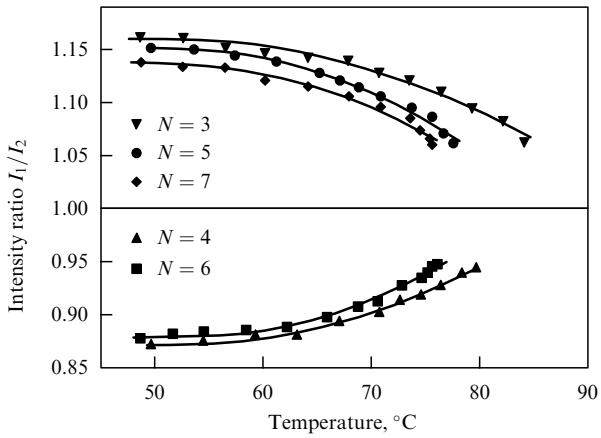


**Figure 2.** The ratio of optical reflections polarized perpendicular ($I_1$) and parallel ($I_2$) to the electric field in the Sm $C^*_A$ phase of thin films with an even and odd number of layers (taken from Ref. [10]). Films with the odd and even number of molecular layers possess transverse and longitudinal electric polarizations, respectively; $N$ is the number of molecular layers in the film.

on the order of 0.2 of the layer polarization [9]. In an electric field, molecules in films with an odd and even number of layers are oriented in different directions [8]. Figure 2 borrowed from Ref. [10] shows the ratio of the intensities of light polarized perpendicular ($I_1$) and parallel ($I_2$) to the electric field direction. In films with an odd number of layers, $I_1/I_2 > 1$ (the plane of molecular tilt is perpendicular to the electric field); in films with an even number of molecular layers, $I_1/I_2 < 1$ (the plane of molecular tilt is parallel to the electric field). These examples demonstrate substantial variation of thin-film polar characteristics compared with bulk samples. Indeed, electric polarization arises in films of nonpolar liquid crystals (Sm $C$), longitudinal polarization in ferroelectric films (Sm $C^*$), and either transverse or longitudinal polarization in thin films of antiferroelectrics (Sm $C^*_A$).

The structure and phase transitions in films of Sm $C$ type liquid crystals can be described with the help of Landau's discrete phenomenological model of phase transitions [11–14]. The film structure is governed by a two-component (2D) vector $\xi_i$, where $i$ is the number of the layer in the film. The free energy of a smectic liquid crystal may be represented in the form of expansion in a power series of structural $\xi$ and polar $\mathbf{P}$ order parameters. Energy minimization with respect to polarization yields the relation between $\xi$ and $\mathbf{P}$. Therefore, the energy may be written down as a function of $\xi$ alone with renormalized expansion coefficients [12, 13]:

$$F = \sum_i \left[ \frac{1}{2} a_0 \xi_i^2 + \frac{1}{4} b_0 \xi_i^4 + \frac{1}{2} a_1 \xi_i \xi_{i+1} + b_1 \xi_i^2 (\xi_{i-1}\xi_i + \xi_i \xi_{i+1}) + f[\xi_i \times \xi_{i+1}]_z \right], \quad (1)$$

where $a_0 = \alpha(T - T^*)$. The first two terms define the Sm $A$ – Sm $C$ transition in isolated layers, while the third and the fourth terms account for interactions between adjacent layers. The interaction related to chirality of molecules is described by the last term of the expansion (the so-called Lifshitz term). Coefficients $a_0$, $b_0$, and $T^*$ for surface layers and for the bulk layers are different; this difference reflects the suppression of fluctuations near the surface and a shift of transition temperature in the films to the high-temperature region. Structures and phase transitions are found by means of numerical minimization of the free energy over the phase and the modulus of the order parameter in all film layers. Interlayer interactions stabilize the synclinic structure (Sm $C$, Sm $C^*$) at negative $a_1$, and anticlinic structure (Sm $C^*_A$) at positive $b_1$. The contribution from the term with the fourth power of $\xi$ to the interlayer interaction energy predominates at low temperatures, leading to a phase transition toward the anticlinic structure. The free energy in the form of Eqn (1) may be used to describe the structure and phase transitions in ferroelectric and antiferroelectric liquid-crystal films of variable thickness. In order to describe more complicated structures with alternating synclinic and anticlinic orientation of adjacent layers or Sm $C^*_\alpha$ structures with a short-pitch helix, it is necessary to introduce additional terms to the energy, namely, frustrational interlayer interaction

$$F_1 = \frac{1}{8} a_2 \sum_i \xi_i \xi_{i+2} ,$$

and an energy barrier between synclinic and anticlinic orientations of molecules:

$$F_2 = a_3 \sum_i [\xi_i \times \xi_{i+1}]^2 .$$

An example of the computation of structures with an experimentally established temperature-dependent phase sequence is presented in Fig. 3 borrowed from Ref. [14]. It is accepted at present that in all smectic liquid crystals with polarly ordered layers only the phase of the order parameter varies from layer to layer, whereas its modulus is the same in all layers of a bulk sample. In thin films, the large value of the order parameter modulus near the surface and the interaction between the phase and the modulus of the order parameter result in the formation of complex structures with the phase and the modulus of the order parameter varying from layer to layer. An important result of computations in works [13, 14] is the prediction of smectic phases in which (even in bulk samples) the modulus of the order parameter differs in various layers.

Second-order phase transitions or weak first-order phase transitions [e.g., Sm $A$ – Sm $C$ (Sm $C^*$)] and phase transitions of the first order are transformed differently in thin films. The Sm $A$ – Sm $C^*$ transition temperature essentially depends on the film thickness [15]; transition to a tilted structure (Sm $C^*$) in the surface layer induces transition to the same structure in the entire film. In the first-order transition between two structures with tilted molecular orientation (e.g., Sm $C^*$ – Sm $C^*_A$ or Sm $C^*$ – Sm $C^*_{FI1}$ – Sm $C^*_A$), the surface transition occurs via a change in the molecular orientation in the surface layer relative to the layer closest to the surface [16, 17]. The transition temperature in a two-layer film is shifted to the high-temperature region by approximately 30 K compared with a bulk sample (Fig. 4) [17]. The number of transitions depends on the film thickness. In films having $N > 4$ molecular layers, transitions break down into high-temperature (near the surface) and low-temperature (in interior layers) branches. In the intermediate temperature range, there appears synclinic interlayer ordering of inner layers, and anticlinic ordering in the two surface layers. Phase transitions in films from an Sm $A$ structure to one with orientationally ordered bonds in the plane of smectic layers (Sm $B$) or to a crystal structure (Cr $B$) as a rule occur in a

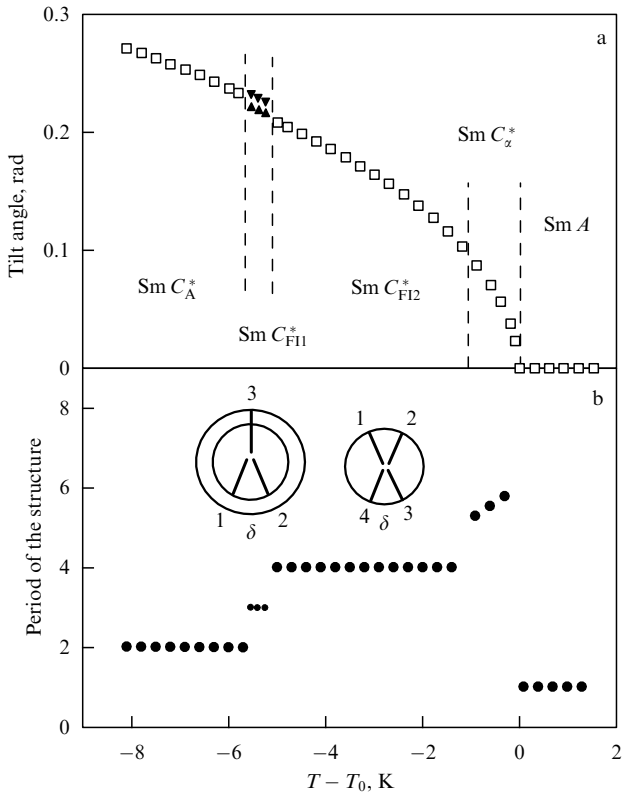


**Figure 3.** Temperature dependence of the tilt angle in radians (a) and the layer ordering period in the number of layers (b) for Sm $C_A^*$ phase, intermediate Sm $C_{FI1}^*$ and Sm $C_{FI2}^*$ phases, and Sm $C_\alpha^*$ structure (short-pitch helix with a period incommensurate with layer ordering). $T_0$ — transition temperature to Sm $A$ phase. Azimuthal orientation of molecules in the nonplanar Sm $C_{FI1}^*$ and Sm $C_{FI2}^*$ structures is shown in the upper part of figure b. Angle $\delta$ of molecular tilt distortion in the layers is due to chirality. Upright and inverted triangles in figure a correspond to layers 3 and 1(2), respectively, in figure b (taken from Ref. [14]).

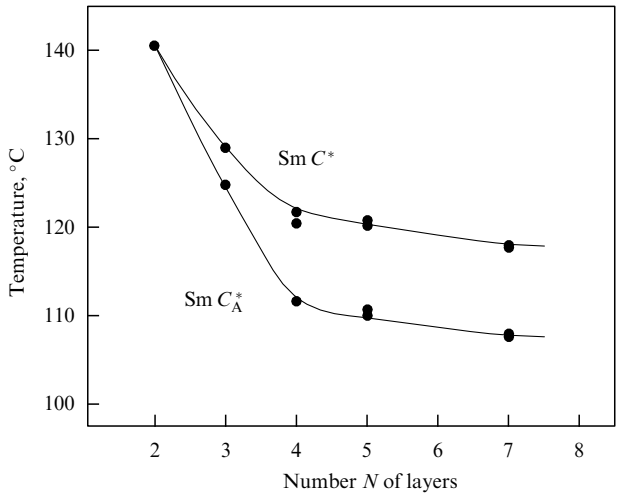


**Figure 4.** Transitions in thin films of a smectic liquid crystal characterized by a sequence of Sm $C_A^*$ – Sm $C_{FI1}^*$ – Sm $C^*$ phase transitions in the bulk (taken from Ref. [17]). $N$ is the number of molecular layers in the film. High-temperature branch fits transitions near the film surface, low-temperature branch — deep inside the film.

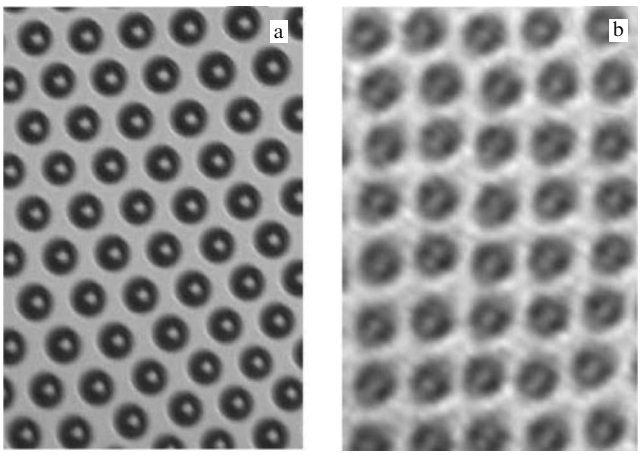


**Figure 5.** Two-dimensional structures — hexagonal (a) and square (b) — produced from nematic droplets in a smectic film (taken from Ref. [27]). Horizontal size of the photos is 115 μm (a) and 40 μm (b).

layer-by-layer fashion [18]. At a temperature some 10 K above phase transition temperature in the bulk, transition to Sm $B$ (or to Cr $B$) takes place only in one surface layer. As the temperature decreases, a series of discrete transitions may occur in molecular layers closest to the surface. Such structures are convenient for investigating two-dimensional crystallization.

## 3. Interaction and self-organization of topological inclusions in smectic films

Liquid crystals are extremely well suited for the experimental investigation and theoretical description of interaction and self-organization of microparticles in anisotropic media [19–27]. The interaction is emerging because these particles cause elastic deformation of the molecular ordering field in a liquid crystal. There is experimental evidence of particle self-organization with the formation of linear chains [19, 21, 23–25], clusters [21, 25], or two-dimensional ordered structures [25–27]. Attraction between particles at large distances and their repulsion at small distances are due to the formation of topological defects in the liquid crystalline medium or at the particle surfaces. Depending on the boundary conditions at the particle surfaces and the size of the particles, interactions between them can be dipole–dipole, quadrupole–quadrupole or even more complicated, including those associated with deformation of smectic layers. By way of example, Fig. 5 displays a photograph of smectic films with particles translationally ordered into two-dimensional hexagonal and square lattices [27].

In smectic $C$-types of liquid crystals, projections of long molecular axes onto the film plane (the so-called **c**-director) form a 2D field of molecular ordering [1]. The rigid orientation of molecules at the particle surfaces in a film leads to the deformation of the **c**-director field. A radial (normal to the particle surface) or planar (parallel to the particle surface) orientation of a **c**-director is simplest to consider. Such an orientation for solid particles can be obtained by depositing a thin orienting layer on their surfaces. Particles of a different phase (liquid, nematic, cholesteric) as a rule orient the **c**-director by themselves, either radially or planarly. The field of molecular ordering in a film containing a particle with radial or planar boundary conditions is analogous to the field created by a point topological defect with the topological charge $S = +1$. The necessity to retain the topological charge in the system

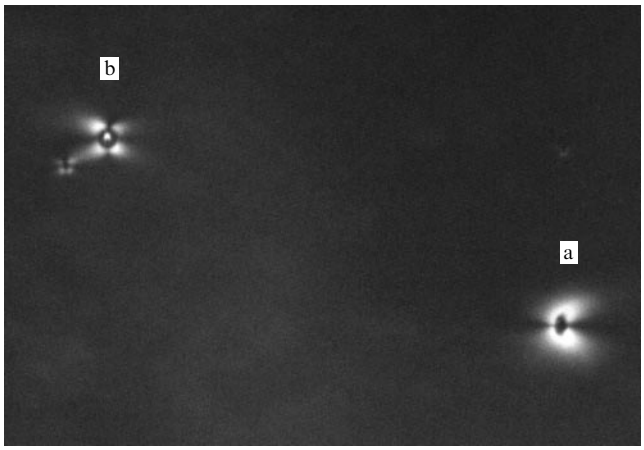


**Figure 6.** Smectic film containing inclusions of nematic droplets with a single point defect ($S = -1$) (a) and two topological defects ($S = -1/2$) (b) at the inclusion surface. Horizontal size of the photos is 680 μm. The orientation of the **c**-director far from the inclusions (in the vertical direction) is uniform. At the droplet boundaries, the **c**-director is oriented parallel to them.

imposes constraints on the deformation of the molecular ordering field in the film. The placement of a particle in the film or its birth in the film (for example, as a liquid drop during film heating) gives rise, close to it or on its surface, to a topological defect or defects with the total topological charge $S = -1$ [22]. The particle and the associated topological defect (defects) make up a topological dipole (quadrupole).

Figure 6 presents a photograph of particles in the film of Sm *C* liquid crystal with the planarly oriented **c**-director at the particle boundaries. Particle 'a' has one point topological defect with the strength $S = -1$ on the left-hand side of the film – particle interface. Particle 'b' has two point topological defects of the strength $S = -1/2$ at its upper and lower boundaries. The total topological charge of each particle equals zero. Particle 'a' constitutes a topological dipole, particle 'b' makes up a topological quadrupole. The configuration of the molecular ordering field near the particles and interparticle interactions may be described using an electromagnetic analogy [22]. The orientation of a **c**-director in a film, described by the solution of the Laplace equation $\Delta\varphi = 0$, may be represented in the form of summarized deformations $\varphi_i$ created by real (physical) and virtual topological defects. Attraction between dipole-type particles (a) leads to the formation of linear chains from particles with the dipole moment parallel to the chain [23, 24]. More complicated structures are formed from particles 'b' with quadrupole – quadrupole interactions. The particles are arranged so as to minimize the elastic strain energy of the **c**-director field. For particles with quadrupole symmetry, four directions (light zones in Fig. 6b) correspond to the energy minimum. Formation of branched chains, clusters or translationally ordered structures was found in experiment [25, 26]. The actual task is to employ self-organization for obtaining structures of various types from micro- and nanoparticles, as well as their rearrangement with the use of external electric and magnetic fields or light-induced effects.

On-going studies of thin smectic films cover a broad spectrum of problems pertaining to different areas of condensed state physics (physics of thin films, surface, low-dimensional 2D and 1D systems, etc.). Further still many studies are currently practicable only on smectic films because ultrathin inorganic films of comparable quality are unavailable. As far as liquid crystals are concerned, studies of thin films have become an important area of investigation into new liquid crystalline materials. Moreover, the structures of many materials were only elucidated in the studies of freely suspended thin films.

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# Electrooptics and photonics of liquid crystals

S P Palto

### 1. Introduction

This report is designed to briefly discuss some promising areas of research concerned with the electrooptics and photonics of nematic liquid crystals with special reference to the effects of bistable switching and lasing effect in chiral nematics.

The physics of liquid crystals (LCs) has been intensively developed in the last half century to provide a basis for their extensive practical application in a variety of electrooptical devices and high-tech products, such as information display systems and flat TV screens. It is worthwhile to note that the progress in LC science has been supported by major