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Focal conic domains with positive Gaussian curvature and saddle-splay rigidity of smectic L_α phases

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We report on the experimental observation of a different type of focal conic domain with positive Gaussian curvature. A particular type of these domains is usually given the name "spherulites." Their appearance is due to a low (probably negative) value of the saddle-splay elastic constant. These domains are observed in the lamellar L_α phase with a low cosurfactant to surfactant (c/s) ratio. The increase of this ratio results in usual focal domains with negative Gaussian curvature. It allows us to conclude that the saddle-splay constant is governed by the c/s ratio, and changes sign from positive to negative when c/s decreases.

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The smectic-A phase or its lyotropic analog, the L_α phase, are phases of liquid layers, which can be conveniently represented by a set of equidistant surfaces. The elastic energy density carried by the layers deformations is associated with their mean curvature $(\sigma_1+\sigma_2)$ and Gaussian curvature $\sigma_1\sigma_2$ [1]:

$$f=\tfrac{1}{2}K(\sigma_1+\sigma_2)^2+\bar{K}\sigma_1\sigma_2\,, \tag{1}$$

where σ_1 and σ_2 are the principal curvatures of the surfaces, and K and $\bar{K}$ are, respectively, the splay and saddle-splay elastic constants. This expression of the free-energy density does not include the interaction energy between layers, and assumes therefore that the layer equidistance is conserved.

The second term of Eq. (1) is responsible for the changes of layer topology. However, despite of the evident importance of the saddle-splay rigidity, up to now there are no general methods for the determination of $\bar{K}$, except for a few cases of special instabilities [2]. As it was shown recently [3], the corresponding information can be extracted from the geometry of focal conic domains (FCD), which are the most general type of topological defects in smecticlike systems where the layer equidistance is conserved [4]. It was found that $\bar{K}$ is positive. On the other hand, in contrast with usual elastic constants like K, there is no opposition in principle to a sign inversion of $\bar{K}$. This paper gives a theoretical analysis of the relation between the saddle-splay contribution to the free energy of the layered system and the topology of the defects in these media.

We also report on the observation of a different type of focal conic domain with positive Gaussian curvature. These findings show the existence of media with a negative saddle-splay rigidity $\bar{K}$.

First of all, let us recall the basic features of the focal conic domains (see also [3,5–8]). The layers within each domain are folded around two conjugated focal lines, viz., an ellipse and a hyperbola, in such a way that everywhere they are perpendicular to the straight lines joining any point of the ellipse to any point of the hyperbola. The physical part of the normal is located either between these two points or outside. It is easy to see that in the first case $\sigma_1\sigma_2<0$, while in the second case $\sigma_1\sigma_2>0$ (Fig. 1). According to the layer location and, consequently, to the sign of the Gaussian curvature, one distinguishes FCD's of the first species ($\sigma_1\sigma_2<0$) and FCD's of the second species ($\sigma_1\sigma_2>0$) [5], abbreviated as FCD-I and FCD-II. In spite of the formal geometrical symmetry of these two classes, up to now only FCD-I are experimentally known starting with the Friedel and Grandjean work [6]. To cast light on the problem in terms of $\bar{K}$ term, let us consider the elastic energy of the FCD-II.

The curvature energy of the FCD-II for media with nonzero $\bar{K}$ can be calculated using Kléman's analytical description [7]. The geometry of each bilayer within the domain is described by rectangular curvilinear coordinates (ω,ν) along the lines of curvature [7]:

$$\sigma_{1,n}=1/(ae\cos\nu-r_n),\quad \sigma_{2,n}=1/(a\cosh\omega-r_n)\,, \tag{2}$$

where $n=1,2,\ldots$ labels the bilayers; a and e are the major axis semilength and the eccentricity of the ellipse, respectively; $r_n=a+d(n-\frac{1}{2})$ is measured along any normal to the bilayers; and d is the interbilayer separation. For the sake of accuracy, we introduce the $d/2$ term in the last ex-

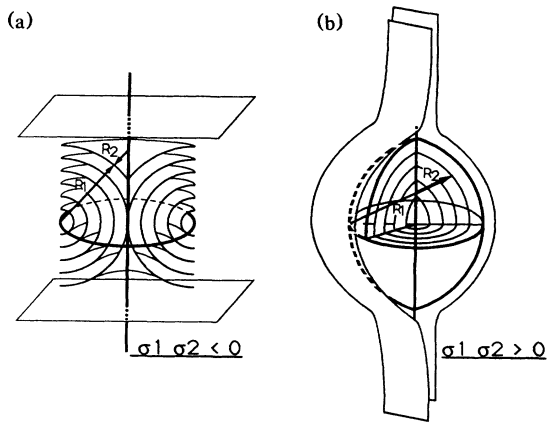

FIG. 1. The focal conic domains with (a) negative and (b) positive Gaussian curvature.

pression of r_n to provide for the natural separation d between the two parts of the first bilayer. However, this correction is negligible when n is large. We will consider here only the experimentally observed case of the rotationally symmetrical domains, $e=0$. The integration of (1) with distribution (2) and $e=0$ over the range $0 \le \nu < 2\pi$, $1 < \cosh\omega < r_n/a$ (which corresponds to $\sigma_{1,n}\sigma_{2,n} > 0$) yields the elastic energy of the focal domain constructed by N bilayers with positive Gaussian curvature

$$W_{K,\bar{K}} = \sum_n^N W_{K,\bar{K},n}$$
$$= 4\pi(2K+\bar{K})R\left[\left(1-\frac{a^2}{R^2}\right)^{1/2} - \frac{a}{R}\arccos\frac{a}{R}\right]$$
$$+ 2\pi K a^2 \sum_n^N \frac{\ln[2d(n-\frac{1}{2})/r_c]}{r_n(r_n^2-a^2)^{1/2}} + W_c , \qquad (3)$$

where $R = a + d(N-\frac{1}{2})$; r_c is a core radius along the hyperbola (here degenerate to a straight line) which may be taken of the order of d, and W_c is a core energy. The latter can be estimated of the order of $K\sin^2\omega$ per unit length of core, where the angle ω is measured between the normal to the bilayer and the defect line, i.e., $\sin\omega = a/r_n$. Thus after the integration over $r_1 \le r_n \le R$ one obtains the total core energy of the line:

$$W_c = \alpha K a^2 (R-r_1)/Rr_1 , \qquad (4)$$

where α is some numerical coefficient of the order of unity. We have deliberately chosen a positive core energy (ignoring any contribution analogous to saddle splay in the core), since we assume that the defects in question are metastable. As it follows from Eqs. (3) and (4), the smallest energy belongs to the spherical domains with $a=0$ and $W_{K\bar{K}} = 4\pi(2K+\bar{K})R$; these domains contain only a point singularity which adds neither a logarithmic contribution to the elastic energy, nor any core contribution.

The establishment of Eq. (3) requires some comments as regards the saddle-splay distribution. Observe that in the $a=0$ limit the saddle-splay term tends to $4\pi\bar{K}R$, as expected for a sphere of radius R. However, one might wonder whether the region outside the FCD-II does or does not contribute to the saddle-splay term. It does not because by construction the layers outside the defect are homotopic to infinite cylinders (in the capillary tubes) or planes (if the sample is prepared between two planar glass plates); hence by Gauss-Bonnet theorem [8] their integrated Gaussian curvature vanishes. Note that the rotational symmetry of the FCD-II defect is broken by the outside layers (this is not so for a FCD-I toroidal defect, which fits more nicely with the outside layers [3]).

The dependency $W(K,\bar{K})$ on $\bar{K}$ is simple and clear: The decrease of $\bar{K}$ favors the appearance of the FCD-II. This behavior is just opposite to the situation with FCD-I, where the elastic energy contains the saddle-splay term of opposite sign in $\bar{K}$ and reads for the case $e=0$ as [3]

$$W_{K,\bar{K}} = 2\pi^2 a[K\ln(2a/r_c) - 2K - \bar{K}] . \qquad (5)$$

To compare the elastic energies for both types of domains which occupy approximately the same volume, it is convenient to put in the last expression (5) $a=R$ and take (3) and (4) with $a=0$. Since the logarithmic term for the FCD-I is usually of the order of 10, one obtains that FCD-II becomes energetically preferable when $\bar{K} < (2-3)K$. This inequality can be only enhanced if one takes into account the nonzero compressibility term W_B: The FCD-II, in contrast with the toroidal FCD-I [3], always deforms the surrounding region and thus changes the bilayer separation outside. Thus the FCD-II total energy $W_{K,\bar{K}} + W_B$ consists of the interior part, which is represented only by a pure curvature energy (the layers keep equidistant) and of the exterior compressibility term. As already emphasized, the Gaussian term does not contribute to the energy of the matrix [Fig. 1(b)]. Omitting the details of the calculations which will be published elsewhere, we have

$$W_B = BR_l^2\lambda(R_l/R_t + R_t/R_l) , \qquad (6)$$

where $\lambda = (K/B)^{1/2}$, B is the layers compressibility modulus, $R_l = (R^2-a^2)^{1/2}$ is the half length of the domain along the symmetry axis, $R_t = R-a$. Thus, as it follows from Eqs. (3)–(6) with $a=0$ in Eqs. (3), (4), and (6), and $a=R$ and $\ln(2a/rc)=10$ in Eq. (5), the spherical-like FCD-II will be preferable to the FCD-I if $\bar{K}$ is smaller than some critical value,

$$\bar{K} \le K(8\pi^2 - 4\pi - R/\lambda)/(2\pi+\pi^2) . \qquad (7)$$

The usual thermotropic materials studied up to now are not obliged to follow condition (7). This can explain why there are no reports on FCD-II in usual liquid crystals [9]. On the other hand, the best candidates for displaying FCD-II seem to be the lyotropic systems in the vicinity of the L_α-L_1 phase transition. This transition shows up in many lyotropic mixtures [10,11] and transforms the lamellar phase L_α with parallel layers and $\sigma_1\sigma_2=0$ to the micellar phase L_1, where $\sigma_1\sigma_2 > 0$ due to the rounded geometry of the elementary units (micellae).

We have studied the L_α phase of the quasiternary system cetylpyridinium chloride (abbreviated as CpCl)–hexanol–brine (1% by weight of NaCl). The weight fraction ϕ_b of brine was within the range 75%–90%. The right choice of the cosurfactant (c, hexanol) to surfactant (s, CpCl) ratio was the main point of importance of the experimental search and was based on the following ideas.

Previous investigations [10,11] have shown that the phase states of the CpCl-hexanol-brine mixture are mainly determined by the c/s ratio. The system exhibits three phases: (1) the L_1 micellar phase with globular or rod-shaped micelles and thus $\sigma_1\sigma_2 > 0$ for low c/s ratios; (2) the lamellar L_α phase with flat bilayers and $\sigma_1\sigma_2=0$ for intermediate c/s ratios; (3) the anomalous isotropic L_3 phase with numerous passages and handles ($\sigma_1\sigma_2 < 0$) for high c/s ratios. Since these states possess different layers topologies, it is reasonable to expect that the essential contribution to the phase transitions comes from the saddle-splay modulus $\bar{K}$ variation, as first proposed by Porte *et al.* [11], keeping in mind that $\bar{K}$ might well change sign from positive to negative within the range L_α phase when one moves from the L_3 to the L_1 boundaries in the phase diagram. Thus to find the region with $\sigma_1\sigma_2 > 0$ and FCD-II

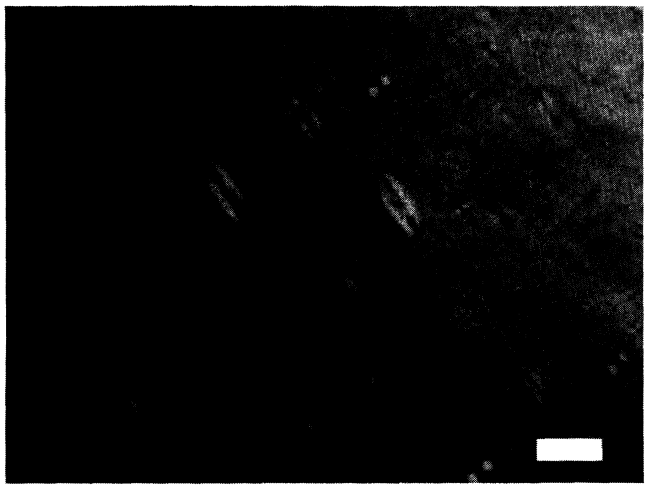

FIG. 2. The texture of the elongated axisymmetrical focal conic domains with positive Gaussian curvature (FCD-II). [CpCl]:[hexanol]:[brine] = 13:7:80. The bar length is 50 μm.

we investigated the L_α phase in the vicinity of the L_α-L_1 transition with c/s=[hexanol]/[CpCl] =0.45–0.6 in weight units (Fig. 3 in Ref. [10]).

The mixture was introduced by capillarity in glass tubes with a rectangular (2 mm×200 μm) or a circular (200 μm) cross section. It orients homeotropically (layers parallel to the glass boundary). Observations were conducted in the polarizing microscope at 25 °C. Immediately after the sample preparation one observes textures which differ drastically from typical textures ever reported for the smecticlike phases. Their main feature is the presence of birefringent elongated domains located at different levels of the surrounding dispersion matrix which is also birefringent (Fig. 2). The domains possess rotational symmetry with longitudinal axis usually oriented along the capillary axis, i.e., parallel to the layers. Within the accuracy of the optical observations the meridian cut of the domain boundary is an arc of circle with radius R greater than the radius R_t of the transversal cross-section of the domain [Fig. 3(a)]. Investigations with quartz wedge indicate that the optical axes and thus the normals to the bilayers are distributed in a radial-like manner and are perpendicular to the domain boundary; there is also a sharp change in their orientation at the domain axis.

The above described peculiarities give evidence that the observed domains are the FCD-II with structure shown in Fig. 1(b). However, the elongated shape of these domains, which is probably induced by the material flows, is not stable. As time elapses the elongated domains relax into spherical ones, while keeping a constant value of the transversal radius R_t (Fig. 3). Eventually one has $R=R_t$. Analogous spherical domains were observed also by Gomati *et al.* [10] for the same phase region of the [CpCl]:[hexanol]:[brine] mixture and are in fact the trivial limit case of the FCD-II with the ellipse shrinked into a point. There are also other observations of spherical domains in lamellar systems, see, e.g., [12,13]; however, in most cases these so-called spherulites were observed to be dispersed in the isotropic matrix rather than in the birefringent one with the periodical lamella stacking, except in Ref. [10], which provides probably the first clear observation of spherulites in a lamellar phase.

The increase of c/s ratio leads to the disappearance of the FCD-II with $\sigma_1\sigma_2>0$ and to the appearance of usual FCD-I with $\sigma_1\sigma_2<0$, which were described in detail for the investigated system in our previous paper [3].

As it is easy to see, the observations unambiguously confirm the theoretical predictions: (a) FCD-II appear instead of FCD-I in the vicinity of the L_α-L_1 transition where $\bar{K}$ is expected to be small or negative [10]; (b) the elongated domains tend to relax into spherical FCD-II. Moreover, since the size of FCD-II is known from the experiment (typically $R\approx 10$ μm), the observations allow us to estimate $\bar{K}/K$ using Eq. (7).

To find $\bar{K}/K$, one should estimate $\lambda=\sqrt{K/B}$. Within the scope of the Helfrich "steric interaction" model [14] B scales with temperature T and interlamellae separation d

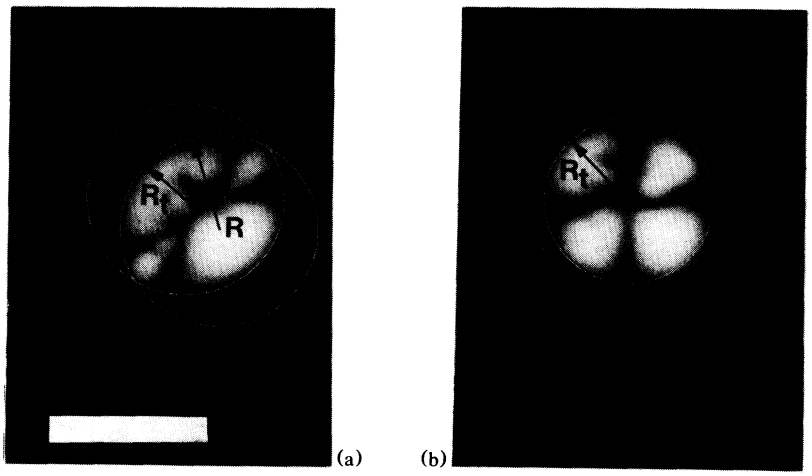

FIG. 3. The shape transformation of (a) the elongated FCD-II to (b) the spherical one. Photo (b) was taken for the same part of the sample 5 h later than photo (a). [CpCl]: [hexanol]:[brine] = 13:7:80. Bar length 50 μm.

as

$$B = 9\pi^2 (k_B T)^2 / 32 k_c d^3 , \quad (8)$$

where $k_c = Kd$ is the lamellae curvature modulus. The latter was measured as the function of the c/s ratio for the [CTAB]:[hexanol]:[brine] system (where CTAB denotes cetyltrimethylammonium bromide) similar to the one investigated here [15]. In the vicinity of the L_α-L_3 phase transition (relatively high hexanol content) k_c was found to increase within the range $(5.5-7)k_BT$ as the c/s ratio decreases. Since the alcohol cosurfactant k_c lowers, one should expect $k_c \sim 10 k_B T$ for low hexanol concentration, in the vicinity of the L_α-L_1 phase transition. Taking this order of k_c and using Eq. (8), one obtains that $\lambda \sim 5d$. As far as the typical interlamellae separation d for 80–90% dilution with brine is 10–30 nm [10], the order of λ magnitude is 10^2 nm [16]. Thus, the condition (7) with typical $R = 10$ μm leads to the estimation $\bar{K} \sim (-2K)$, i.e., $\bar{K}$ is negative.

In principle, the last rough estimation is close to a lowest possible value of $\bar{K}$ within the range of the L_α phase [11]. With a smaller $\bar{K}$ the system of parallel flat layers can be unstable with respect to the spherical-like packing. An numerical analysis of the FCD-II total energy $W_{K,\bar{K}} + W_B$ as a function of the number N of bilayers with $\bar{K} < -2K$ and expected $\lambda/d = 1-20$, $r_c/d = 0.5-2$ shows that the lowest energies of the FCD-II are negative, i.e., smaller than the energy of the flat layer packing, which can be taken as zero. So, one can expect that the FCD-II may serve as the nucleus of a new phase during the transition from the L_α state with zero Gaussian curvature to a phase consisting of spheres with positive curvature. We will discuss the relation between the FCD's and the phase diagrams in detail in a forthcoming article.

Let us summarize our findings and conclude. First, we have observed a special type of focal conic domain, FCD-II, which possesses a positive Gaussian curvature of the lamellae, while the usual FCD-I has a negative one. Besides this, the FCD-I and FCD-II differ in the symmetry of surrounding matrix. The theoretical analysis shows that the stability of the FCD-II and FCD-I crucially depends on the value and sign of the saddle-splay constant $\bar{K}$. Both experiment and theory reveal that the elongated FCD-II are unstable and tend to transform into spherical FCD-II. Second, the FCD-II were observed in that region of the lamellar L_α phase which is characterized by a low cosurfactant-to-surfactant ratio. With higher content of the cosurfactant one observes the usual FCD-I. This allows us to conclude that $\bar{K}$ is really governed by the c/s ratio, and decreases with the decrease of the cosurfactant concentration, as it was predicted by Porte *et al.* [11]. Our estimations give a negative sign of $\bar{K}$ for the hexanol-poor L_α phase, $\bar{K} \sim -2K$, while for the hexanol-rich region the previous data [3] give a positive sign, $\bar{K} \sim (6-10)K$.

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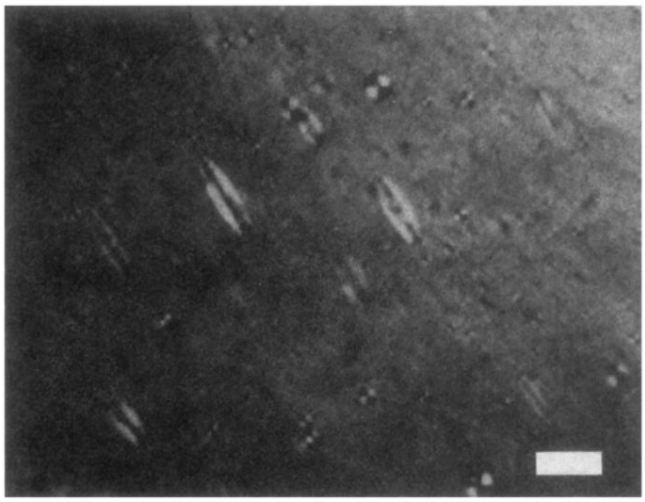

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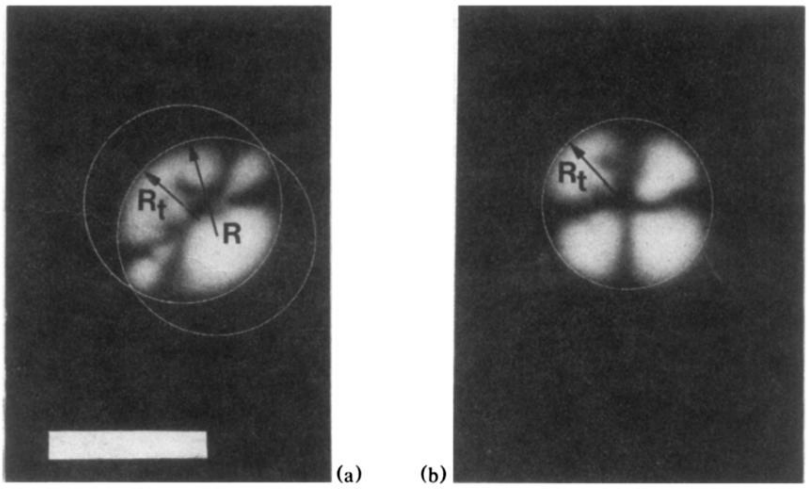

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