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Oleg Lavrentovich  
Kent State University - Kent Campus, olavrent@kent.edu

V. M. Pergamenshchik  
Kent State University - Kent Campus

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Stripe Domain Phase of a Thin Nematic Film and the $K_{13}$ Divergence Term

O. D. Lavrentovich$^{1,2,*}$ and V. M. Pergamenshchik$^{1,*}$

$^1$Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
$^2$Department of Physics, Kent State University, Kent, Ohio 44242

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To verify the status of the divergence $K_{13}$ term in the elastic theory of liquid crystals we study submicron films placed onto an isotropic fluid substrate in the Langmuir trough (Langmuir liquid crystal, LLC). The upper and lower surfaces favor normal and tangential molecular orientation, respectively. The periodic domain phase is observed in a nematic LLC. The dependence of the periodicity $L$ of the domains vs film thickness $h$ can be explained only if the elastic energy is accompanied by divergence terms with nonzero constants $K_{13}$ and $K_{24}$. It is found that for $5CB$ $K_{13} = -0.2K_{11}$.

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Introduction.—Nematic liquid crystal films with submicron thickness $h \sim 0.1-1 \mu m$ placed onto an isotropic substrate represent a unique soft-matter system [1–6]. In comparison with Langmuir monolayers the films are thick enough to demonstrate the role of intrinsic liquid crystalline order in the interplay between molecular structure and macroscopic organization. At the same time, the films are thin enough for a competition between the surface and bulk properties that results in a number of very unusual patterns [1–4,6]. The patterns are strongly influenced by divergence elastic terms in the nematic free energy. In particular, the stripe domain structure discovered in the films [1,2] was the first effect observed that is driven by the divergence $K_{24}$ term [2,5]. In this Letter we show that the stripe domain phase can be quantitatively described only with regard for the second divergence contribution, the so-called $K_{13}$ term, which has been for decades a source of confusion in the physics of liquid crystals.

Divergence free energy terms which can be introduced in the Landau-type approach to different condensed matters (e.g., liquid crystals, superfluid $^3$He-B, ferromagnets) are usually omitted. Liquid crystals present a unique situation where divergence terms are found to be in fact meaningful. The conventional nematic free elastic energy $F_2$ quadratic in the director derivatives $\partial n$,

$$F_2 = \int dV [f_F - K_{24} \nabla(n \nabla n) + n \times \nabla \times n + K_{13} \nabla(n \nabla n)],$$

contains the Frank sum $f_F$ of the standard bulk terms (splay $K_{11}$, twist $K_{22}$, and bend $K_{33}$), and also the $K_{24}$ and $K_{13}$ divergence terms [7]. For a long time both divergence terms have been disposed because of certain mathematical difficulties (see e.g., [5]). Only recently the $K_{24}$ term was shown to give no ambiguity [8–10] and even $K_{24}$ was estimated experimentally both for nematic [6,11–13] and smectic [14] phases. The remaining central problem of the elastic theory is the $K_{13}$ problem.

The $K_{13}$ problem derives from the fact that the functional (1) is not bounded from below unless $K_{13} = 0$ [10,15]. There is, however, no fundamental reason why $K_{13}$ should vanish [9,16,17]. If $K_{13} \neq 0$, then the energy can be bounded by terms of higher order in derivatives [16]. If the number of the higher order terms is finite, the theory predicts strong subsurface deformations [9,16,18] which are rather difficult to accommodate in the continuum approach. To avoid these unphysical deformations, it was suggested [19] that the finite-order theory is equivalent to the conventional theory [7] where in Eq. (1) $K_{13} = 0$ but the interfacial energy of the sample boundary (anchoring energy) is renormalized.

Alternative infinite-order approach [10] shows, however, that the deformations can be restricted to the standard weak magnitude by the infinite sum $R_{\infty}$ of all higher order terms in the expansion of the elastic energy. The family of the director distributions in the infinite-order approach satisfies the Euler-Lagrange equations for the functional $F_2$ alone (the same family of $n$ was proposed a priori in [20]). As a result, no information on the higher order terms enters observable quantities (in contrast to the theory [9,16,18]). Therefore, in the infinite-order approach the $K_{13}$ problem is reduced to the experimental measurement of $K_{13}$. The most favorable situation would be the one where the divergence terms are involved in the formation of different equilibrium states, and the dilemma $K_{13} = 0$ or $K_{13} \neq 0$ could be resolved by a comparison of experiment and theory. A most appropriate object seems to be a hybrid aligned nematic film with azimuthally degenerate boundary conditions [1–5].

In a hybrid film, $n$ depends on the coordinate $z$ normal to the film since the surfaces favor different alignments. The homogeneity of the problem suggests that $n$ is independent of the in-plane coordinates $x$ and $y$ (homogeneous state, HS). However, this naive translational symmetry of the HS can be spontaneously broken by the $K_{24}$ term [2,5] and the stripe domains (SD's) are formed for sufficiently thin films; these in-plane distortions cost no azimuthal anchoring energy since
the ambient media (fluid and air) are isotropic. The
domain periodicity \( L \) is very sensitive to the film thickness \( h \) [2], \( K_{24} \) [5], and, can be expected, to \( K_{13} \), too.

A quantitative study with spreading films was im-
possible because of the nonflat film profile [1,2,6]. In the
present experiment using the Langmuir technique, we
have succeeded in preparation of thin and flat nematic
films which we denote Langmuir liquid crystal (LLC)
films. The most important result is that the experimental
spectrum \( L(h) \) can in no way be explained if \( K_{13} = 0 \). We
found \( K_{13} = -0.2K_{11} \) for 5CB (pentylyenobiphenyl).

Experiment.—The LLC films were prepared in a clean
room (class 100). The Langmuir trough 601M (Nima
Technology Ltd.) was filled with glycerin (99.5+\% purity,
Aldrich Chemical Company, Inc.). Liquid crystal 5CB
(EM Industry, Inc.) was dissolved in hexane (99+\% purity,
Aldrich). The solution was overlaid on the glycerin
surface using microsyringes. Films of 5CB formed after
evaporation of the solvent. The thickness \( h \) of the film
was calculated from the concentration and amount of the
solution and the surface area of the film. Using different
amounts of solution and moving the barriers of the trough
we changed \( h \) in the range 0.14–2.0 \( \mu \text{m} \). The trough
was covered to prevent contamination and mounted on the stage
of polarizing microscope. The temperature was fixed at
23.5 \( \pm 0.3 \) \(^{\circ}\text{C} \).

The film was hybrid alignment since the glycerin favors
tangential orientation, while the free surface of
5CB sets normal orientation [21]. We independently measured
the Rapini-Papoular anchoring coefficient \( \omega \) at
the 5CB free surface using a 2-mm thick nematic sample and employing the method described in [22]:
\( \omega = (1.0 \pm 0.5) \times 10^{-5} \text{J/m}^2 \).

Within the range \( h = 0.14–0.49 \text{ } \mu \text{m} \) the nematic LLC films have periodic-in-plane distortions of \( n \) (SD’s) similar to that described for nonflat spreading films [1,2]. The
difference is that the periodicity \( L \) of the SD’s in
the LLC’s is nearly uniform for the same film as well as for
different films of equal \( h \), (Figs. 1 and 2), while in the
spreading films with nonflat profile [1,2] \( L \) varied from
point to point by more than 20 times.

The experimentally measured SD period \( L \) is a mono-
tonically decreasing function of \( h \) (Fig. 1) and exhibits the
critical thickness \( h_c \approx 0.49 \mu \text{m} \) that restricts the range of the
SD phase from above in accordance with theory [5].

Although the SD phase is attributed to a geometry with essentially submicron scale, \( h = 0.14–0.49 \mu \text{m} \), its
manifestation is detected at supramicron scales \( 5 < L < 200 \mu \text{m} \).
The supramicron \( L \) allows one to disregard the
flexoelectric interaction between the domains since the
Debye screening length (~0.1–1 \( \mu \text{m} [23] \)) is considerably
smaller than \( L \) and the flexopolarization is screened.

Another very important advantage is the smallness of the dimensionless wave number \( \chi = 2\pi h/L \), the only small parameter in the theory [2,5] of the SD phase: the largest \( \chi \approx 0.15 \) occurs for \( h = 0.14 \mu \text{m} \), while for \( h \approx 0.2 \mu \text{m} \) one has \( \chi \approx 0.05 \).

Theory.—Let us consider the nematic layer parallel to the
\((x,y) \) plane normal to the \( \alpha \) axis. The lower
\( z = 0 \) (“1”) and upper \( z = h \) (“2”) surfaces impose, re-
spectively, tangential and normal orientations degenerate
in the \((x,y) \) plane. In the standard parametrization
\( \mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \), where \( \phi \) is the angle
between \( \mathbf{n} \) and the \( x \) axis, and \( \theta = \arctan(n_y/n_x) \), the
HS is described by \( \theta = \theta(z), \phi = 0 \). If the anchoring is
stronger on the tangentially orienting surface \( W_1 > W_2 \),
and the film is thinner than \( h_c = (L_2 - L_1)(1 - p_\perp) [24] \),
then the HS is undistorted in the vertical plane: \( \theta(z) = 2\pi/2 [25] \).
Here \( L_1 = K_{11}/W_1, L_2 = K_{11}/W_2, \) and \( p_\perp = 2K_{13}/K_{11} \).

In the approximation \( K_{11} \approx K_{13} \) the HS is completely
determined by the formula
\( \theta(z) = (\theta_2 - \theta_1)z/h + \theta_1 \),
where \( \theta_1, \theta_2 \) are the solution of the system [10]

\[
2(\theta_2 - \theta_1) + \frac{h}{L_2} \sin2\theta_2 = p_\perp\left[(\theta_2 - \theta_1) \cos2\theta_2 + \frac{1}{2} \sin2\theta_2 - \frac{1}{2} \sin\theta_1\right],
\]

\[
2(\theta_1 - \theta_2) - \frac{h}{L_1} \sin2\theta_1 = p_\perp\left[(\theta_1 - \theta_2) \cos2\theta_1 + \frac{1}{2} \sin2\theta_1 - \frac{1}{2} \sin2\theta_2\right].
\]

For sufficiently small \( h \) the HS becomes unstable with respect to SD’s with periodic perturbations \( \delta \mathbf{n} \) in the form
\( \mathbf{\delta n} = \sum f_i(z) \sin(q_i y), \mathbf{n} = \sum g_i(z) \cos(q_i y) [5] \).

Although \( \delta \mathbf{n} \) contains two twists (about the \( z \) and \( y \) axes), the SD’s appear for any value of \( t = K_{22}/K_{11} \) (in contrast to the periodic Fréederickz effect [26] that requires
small \( t \) and are driven by the \( K_{24} \) mechanism of chiral
symmetry breaking [2,5]. The whole SD spectrum was
shown [5] to be long wavelength (\( \chi \ll 1 \)) if \( t > 0.5 \). It
is just our case: in the experiment \( \chi \ll 1 \), and \( t \sim 0.6 \) for
5CB [27,28].

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The presence of the $K_{13}$ term affects the dependence $\theta_1(h)$ which can be obtained from Eqs. (2) numerically both for $K_{13} = 0$ and $K_{13} \neq 0$.

Functional (3) describes a periodic nonlinear wave $G(u)$ [5] with the wave number

$$\chi = 2\pi h/L = \sqrt{-0.4D\lambda/3P},$$

where the coefficient 0.4 results from nonlinear interaction of the harmonics.

The spectrum $\chi(h)$ exists when $D < 0$ since $\lambda > 0$, $P > 0$ [5]. Hence $D < 0$ and $D > 0$ correspond to the SD’s and HS, respectively [5]. The inequality $D < 0$ holds for $h < h_D$, where $h_D$ is defined by $D(h_D) = 0$. The second restriction comes from Eq. (3): the SD’s with $\chi \ll 1$ do not exist for $Q \leq 0$ since in this case $\min F(G(u))$ corresponds to $\chi \rightarrow \infty$. The inequality $Q > 0$ takes place for $h < h_Q$, where $h_Q$ is defined by $Q(h_Q) = 0$. Thus the upper boundary $h_c$ of the long-wavelength SD phase is obviously $h_c = \min(h_D, h_Q)$. If $h_D < h_Q$ and thus $h_c = h_D$, then at the right end of the spectrum $L(h) \propto \chi^{-1}$ diverges as $(h_D - h)^{-1/2}$ which is illustrated by curves 1–3 in Fig. 2(a), and 3–5 in Fig. 2(b); if $h_D > h_Q$ and hence $h_c = h_Q$, then $L(h)$ drops down abruptly, see curves 4,5 in Fig. 2(a), and 1,2 in Fig. 2(b). There is another region, $h \sim h_a$, where the dependence $L(h)$ becomes steeper [5]. In the experiment such steeping is observed at the left end of the spectrum (Fig. 2) which implies that $h_a \approx 0.15 \mu m$.

The cause for the long-wavelength SD’s is the term in the free energy which functionally coincides with the $K_{24}$ term [2,5] and is proportional to $p_{11} = \left[1 - (2K_{24} - K_{13})/K_{11}\right]$. Therefore, the larger $p_{11}$ the broader the range where SD’s exist. However, if large $p_{11}$ favors SD’s with large $\chi$, it might actually narrow the range of the long-wavelength SD’s with $\chi \ll 1$. Indeed, an increase of $p_{11}$, $L_1$, and $L_2$ results in some increase of $h_D$. At the same time, however, it causes a substantial decrease of $h_Q$. As a result, the upper end $h_c$ of the long-wavelength spectrum is essentially bounded. The maximum possible $h_c$ obviously corresponds to $h_c = h_Q = h_D$ [curve 2, Fig. 2(b)]. Negative $K_{13}$ favors a growth both of $h_Q$ and $h_D$, and thus of $h_c$.

The experimental data $L_{\text{exp}}(h)$ enables one, in principle, to find not only $K_{13}, K_{24}, $ $W_1$ which are not known but $W_2$ as well which can be compared with $W_{2,\text{exp}}$. Note that since the temperature of the film is 10 K below the nematic-isotropic transition point $T_{N-I}$, one can disregard the effects related to variations of the scalar order parameter.

**Comparison of the experimental and theoretical spectra.** — The parameters of the theoretical curve $L(h)$ are $L_2$, $h_a$ (or $L_1$), $p_{11}$, $p_{11}$, and $t$; $K_{11}$ enters only the factor of
the total free energy and does not affect $L(h)$. First we numerically solved Eqs. (2) to obtain their solution $\theta_1$, $\theta_2$ as a function of the parameters indicated. With known $\theta_1$, $\theta_2$ we obtained $\lambda$, $D$, $P$, $Q$, $h_D$, $h_0$ and calculated the spectrum $L(h)$ from Eq. (4).

We found that variations of $t$ about 0.6 affect the spectrum only slightly. Numerical calculations show that the principal problem is to fit to the experimental data at both ends of the spectrum. Our first idea was to reproduce $L_{\text{exp}}(h)$ for $K_{13} = p_{\perp} = 0$. We found it impossible.

(1) $K_{13} = 0$, Fig. 2(b). For $h_0$ from the interval $0.05 < h_0 < 0.1 \mu m$ the theoretical curve $L_{\text{theo}}(h)$ can be made very similar to $L_{\text{exp}}(h)$ at its left end. However, these values of $h_0$ are too small to reach $h_c \sim h_{c,\text{exp}} = 0.49 \mu m$. Indeed, for $L_2 = 1 \mu m$, $h_0 = 0.09 \mu m$, $p_{\parallel} = 1.6$ (curve 1) we have a satisfactory fit to $L_{\text{exp}}(h)$ for $h < h_0 \equiv 0.2 \mu m$, but above $h = 0.2 \mu m$ the SD's do not exist at all. For larger $p_{\parallel}$ and $L_2$ the value of $h_0$ is even smaller. Though $h_0$ increases as $p_{\parallel}$ and $L_2$ decreases (curve 2), this growth is accompanied by a decrease of $h_D$. At last at $p_{\parallel} = 1.2$ a very small decrease of $p_{\parallel}$ (from 1.2 for the curve 2, to 1.187 for the curve 3) makes $h_D < h_0$, and the end $h_c$ of the spectrum appears at $h_D$ rather than at $h_0$. Thus, for $h_0 \sim 0.1 \mu m$ a maximum $h_c$ is only $=0.33 \mu m$ which corresponds to curve 2. On the other hand, we can reach $h_0 > h_0 > 0.49 \mu m$ by taking $h_0$ considerably larger than $h_{c,\text{exp}} \leq 0.15 \mu m$ (curves 4 and 5), but such spectra differ drastically from $L_{\text{exp}}(h)$. If $W_2 \sim W_{2,\text{exp}}$ (curve 4), then $L_{\text{theo}} \ll L_{\text{exp}}$. To get a satisfactory fit at least for $h \sim (0.4 - 0.5) \mu m$, one must allow for $W_2$ an order of magnitude larger values than $W_{2,\text{exp}}$ (curve 5). Since curves 1–5 represent the best fit possible for $p_{\perp} = 0$, we have to conclude that no values of the parameters $L_2$, $p_{\parallel}$, and t allow one to reproduce $L_{\text{exp}}(h)$ even roughly when $K_{13} = 0$.

(2) $K_{13} \neq 0$, Fig. 2(a). For $K_{13} < 0$ we find a narrow range of $p_{\perp}$, $p_{\parallel}$, $L_2$, and $h_0$, where $L_{\text{theo}}$ (h) fits $L_{\text{exp}}(h)$ well: $-0.46 \leq p_{\perp} \leq -0.36$ (i.e., $-0.23 \leq K_{13} \leq -0.18$), $0.95 \leq p_{\parallel} \leq 1.05$, $0.7 \leq l_1 \leq 0.8 \mu m$, $0.8 \leq L_2 \leq 0.9 \mu m$, $0.6 \leq t \leq 0.7$. The best fit is achieved for $p_{\perp} = -0.41$, $p_{\parallel} = 1.0$, $L_1 = 0.76 \mu m$, $L_2 = 0.86 \mu m$, and $t = 0.63$. Curve 1 for this curve $h_c = h_D = 0.49 \mu m$ while $h_0 = 0.50 \mu m$. Other curves in Fig. 2(a) illustrate a high sensitivity of the theoretical curve to small variations of $K_{13}$. In terms of the original variables the best fit corresponds to $K_{13} = -0.205K_{11}$, $K_{22} = 0.623K_{11}$, and the two values of $K_{24}$, $K_{24} = -0.10K_{11}$ and $K_{24} = 0.90K_{11}$ (notice that $K_{24} = 0.90K_{11}$ is very close to the results of Refs. [6, 11–13]. Taking $K_{11} = 6.3 \times 10^{-12}$ N [27] we obtain also the anchoring constants $W_1 = 8.3 \times 10^{-6}$ J/m$^2$ and $W_2 = 7.3 \times 10^{-6}$ J/m$^2$ the latter agrees with the experimental finding, $W_2 = (10 \pm 5) \times 10^{-6}$ J/m$^2$.

In conclusion, the preparation of the nematic LLC's and the measurements of the SD period vs film thickness have allowed us to verify the elastic theory of the SD phase that incorporates both the $K_{13}$ and $K_{24}$ terms. The data can be explained only for $K_{13} \neq 0$: $K_{13} = -0.205K_{11}$ provides a very good description of the experiment; deviations from the range $-0.23 \leq K_{13}/K_{11} \leq -0.18$ lead to a substantial disagreement with the experiment; for $K_{13} = 0$ the disagreement is drastic.

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*[a] Also with the Institute of Physics, Kyyv, Ukraine.

25. For $W_2 > W_1$ the SD’s are suppressed, Ref. [5].
FIG. 1. Stripe domain (SD) phase of a nematic (5CB) film placed on the glycerin substrate for different thicknesses \( h \): (a) \( 0.44 \ \mu m \); (b) \( 0.32 \ \mu m \); (c) \( 0.16 \ \mu m \). The length of the short side of the figure is 240 \( \mu m \).