

Landau theory applied to antiferroelectric ordering in ferroelectric nematic liquid crystals

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The polarization and mass density modulation associated with antiferroelectric ordering in two ferroelectric nematic liquid crystals, a prototypical single compound (referred to as DIO) and a commercial mixture (FNL919), are studied experimentally as a function of temperature. The wave number of the polarization modulation, q_A , is determined by small-angle x-ray diffraction from the weak, accompanying density wave (wave number $q_S = 2q_A$) using a conventional laboratory source. Combined results for q_S and the saturated value of the polarization are analyzed in terms of Landau theory previously developed to describe the paraelectric/antiferroelectric/ferroelectric sequence of phase transitions in solid ferroelectrics. The analysis of q_S indicates that the polarization modulation can be reasonably well approximated by a simple sinusoid in DIO, whereas in FNL919 a sharp decrease in q_S close to the antiferroelectric to ferroelectric transition indicates development of a solitonlike profile.

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I. INTRODUCTION

Since the first reports on the synthesis and characterization of highly polar liquid crystals exhibiting ferroelectricity in a fluid nematic state [1–5], there has been an explosion in discovery of related phases that constitute an ever-expanding “ferroelectric nematic realm” [6–20]. Among the most intriguing is an intermediate, antiferroelectric (AF) phase observed in certain compounds over a range of temperatures between the ordinary paraelectric nematic (N) and ferroelectric nematic (N_F) phases.

Key structural features of the intermediate phase were established in the ferroelectric nematic compound 2,3',4',5'-tetrafluoro[1,1'-biphenyl]-4-yl-2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate (DIO) [2] by Chen *et al.* [9], who performed resonant carbon-edge and off-resonant small-angle x-ray scattering (SAXS) experiments utilizing synchrotron sources. They demonstrated that the polarization field $\vec{P}$, which points along the axis of the nematic director $\hat{n}$, alternates with wave vector $\vec{q}_A$ in a direction normal to $\hat{n}$. The polarization modulation is accompanied by a weak, smecticlike mass density wave, with wave vector $\vec{q}_S = 2\vec{q}_A$. These experimental results were preceded by theoretical [21] work on a modulated splay nematic (N_S) phase that was

initially assigned to the N_F phase in the compound RM734 [3] and by a separate study using Landau mean-field theory to identify the intermediate phase in DIO as a modulated, antiferroelectric phase [22].

The measured value of $q_S = 2q_A \simeq 0.7 \text{ nm}^{-1}$ in DIO implies a spatial period $\Lambda_A = 2\Lambda_S \simeq 18 \text{ nm}$ for the polarization modulation, which varies only weakly over the $\sim 15^\circ\text{C}$ range of the antiferroelectric phase. Synchrotron x-ray measurements of Λ_S and Λ_A on the nanometer scale, also with $\Lambda_A = 2\Lambda_S$, were reported by other investigators [23] in a homologous series based on RM734 [1], the compound in which the N_F phase was first unambiguously identified [4].

The combination of nanoscale density and polarization modulations with commensurate wave vectors along a common axis perpendicular to $\hat{n}$ motivated the designation of a “smectic- Z_A ” (SmZ_A) phase, where “ Z ” denotes tilt of $\hat{n}$ at 90° angle relative to the layer normal ($\hat{q}_S$) and “ A ” refers to the antiferroelectric order. Observations of chevron deformation in the layer structure [9], together with studies of Grandjean textures in samples containing a chiral additive [24], Freedericksz transition experiments [25], and light scattering measurements on layer/director fluctuations [26], indicate that the density/polarization modulation in DIO is one dimensional.

The present work reports on a quantitative comparison of the temperature dependence of the polarization magnitude and mass density wave number q_S in two ferroelectric nematics—the prototypical compound DIO and a proprietary mixture FNL919—to a Landau theory originally developed to describe the paraelectric/antiferroelectric/ferroelectric transitions in solid ferroelectrics [27–30]. This theory was first invoked and applied to study ferroelectric nematics by Chen *et al.* [9] in their seminal paper on DIO. In addition to the

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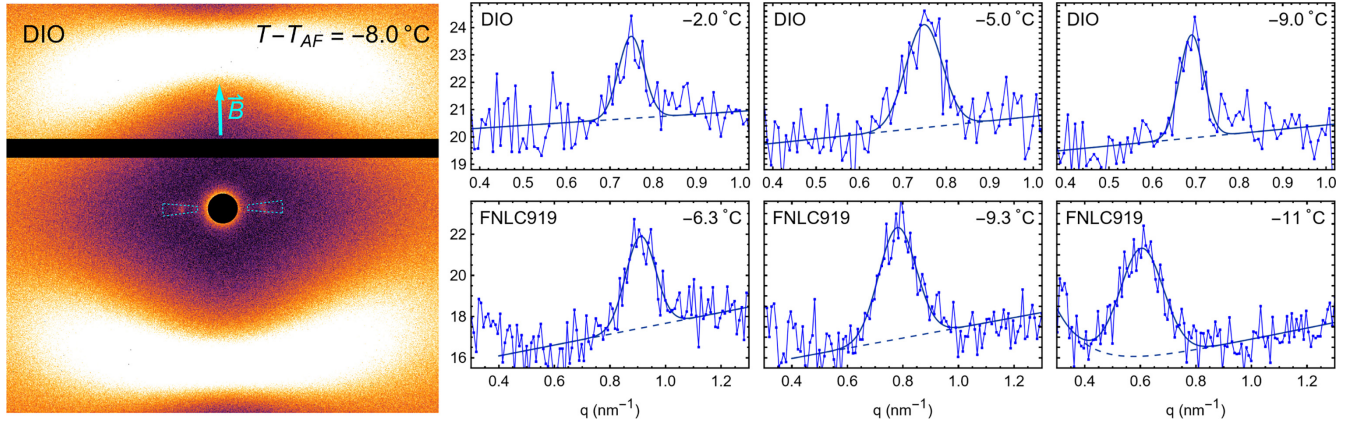


FIG. 1. Left: Representative small-angle 2D x-ray diffraction pattern taken on DIO in the middle of the antiferroelectric phase (at temperature $T - T_{AF} = -8.0^\circ\text{C}$ relative to the paraelectric to antiferroelectric transition temperature). The direction of the magnetic field $\vec{B}$ aligning the collinear director and polarization fields is indicated by the cyan arrow. The pair of weak Bragg spots surrounded by dashed annuli correspond to the first harmonic of the smectic- Z_A layering (period 8.9 nm). Right: Representative plots of SAXS intensity vs scattering wave number q in the antiferroelectric phase of DIO and FNLC919, after azimuthal averaging over the annular regions indicated on the SAXS pattern. The corresponding values of $T - T_{AF}$ are given in the upper right corners. The smooth lines are fits to a Gaussian lineshape, with peak value at wave number q_S , superposed on a slowly varying background function $B(q)$ shown by dashed lines (see Sec. S3 of the Supplemental Material [40]).

variation of the polarization magnitude with temperature, the theory successfully describes two distinct limits in the behavior of $q_S = 2q_A$ observed within the antiferroelectric phase: weakly temperature dependent q_S in DIO, corresponding to a nearly pure sinusoidal polarization modulation, and a sharply decreasing q_S close to the antiferroelectric to ferroelectric transition in FNLC919, indicating an evolution from sinusoidal to solitonlike modulation.

II. EXPERIMENTAL DETAILS

The liquid crystal DIO was synthesized at Kent State University and purified to isolate the *trans* isomer. FNLC919 was provided by Merck Electronics KGaA. Both materials exhibit the phase sequence $N\text{-AF}/\text{Sm}Z_A\text{-}N_F$ on cooling with respective transition temperatures $T_{AF} = 84.0$ and $T_F = 67.7^\circ\text{C}$ for DIO and $T_{AF} = 41.3$ and $T_F = 29.4^\circ\text{C}$ for FNLC919.

X-ray diffraction was conducted using a Xeuss 3.0 small/wide-angle x-ray scattering instrument (Xenocs, Inc.) with a microfocus CuK_α source and a vacuum sample chamber equipped with a hot stage. The samples were contained in sealed, boron-rich glass capillaries (2 mm inside diameter, 10 μm wall thickness). Two-dimensional diffraction patterns were recorded with a 2 h acquisition time at fixed temperatures in the antiferroelectric phase after cooling from the paraelectric nematic phase, where the director was uniformly aligned by an applied magnetic field $\vec{B}$. The incident beam size was $0.9 \times 0.9 \text{ mm}^2$.

Sandwich cells with syn-parallel rubbed, polyimide alignment layers were employed in the measurement of the polarization as a function of T . The sample thickness was 10 μm , and the filled cells were epoxy sealed around the edges. An in-plane, alternating electric field (with triangular wave form and frequency 50 Hz) was applied along the rubbing direction, and the induced polarization current associated

with polarization reversal was recorded as a function of time. Typical fields required to saturate the current varied from 0.1 V/ μm in the lower to 1 V/ μm in the upper antiferroelectric range. Further details are provided in Figs. S2 and S3 of the Supplemental Material [40].

III. RESULTS

Figure 1 shows a small-angle two-dimensional (2D) x-ray diffraction pattern taken on DIO at $T - T_{AF} = -8.0^\circ\text{C}$ (near the middle of the antiferroelectric phase). The intense, diffuse arcs at larger angle and centered along the direction of $\vec{B}$ are associated with skewed “cybotactic” clusters of molecules that are characteristic of short-range positional correlations observed in the N and N_F phases. Along the direction normal to $\vec{B}$, and at smaller angle, are a pair of weak Bragg spots detected only in the antiferroelectric phase that confirm an electron density modulation running normal to the director and polarization fields and demonstrate that smectic- Z_A layering can be detected using a conventional x-ray source [31]. The corresponding value of $q_S = 0.706 \text{ nm}^{-1}$ (period $\Lambda_S = 8.90 \text{ nm}$) closely matches the value 0.705 nm^{-1} from the prior synchrotron x-ray measurements on DIO at the same temperature [9].

Figure 1 also displays representative plots of the scattered x-ray intensity (I_s) from the smectic- Z_A density wave versus q for selected temperatures. The intensity was averaged azimuthally over a $\pm 6^\circ$ range about the axis of the density wave, as indicated by dashed annuli in the SAXS pattern. Peaks at wave number q_S , though quite weak, are clearly distinguished above the background in Fig. 2. Fits of the peaks to a Gaussian profile, $A \exp[-(q - q_S)^2/\Delta q^2] + B(q)$, were used to obtain values of q_S . Here, $B(q)$ is a smooth function that models the background (see Sec. S3 of the Supplemental Material [40]).

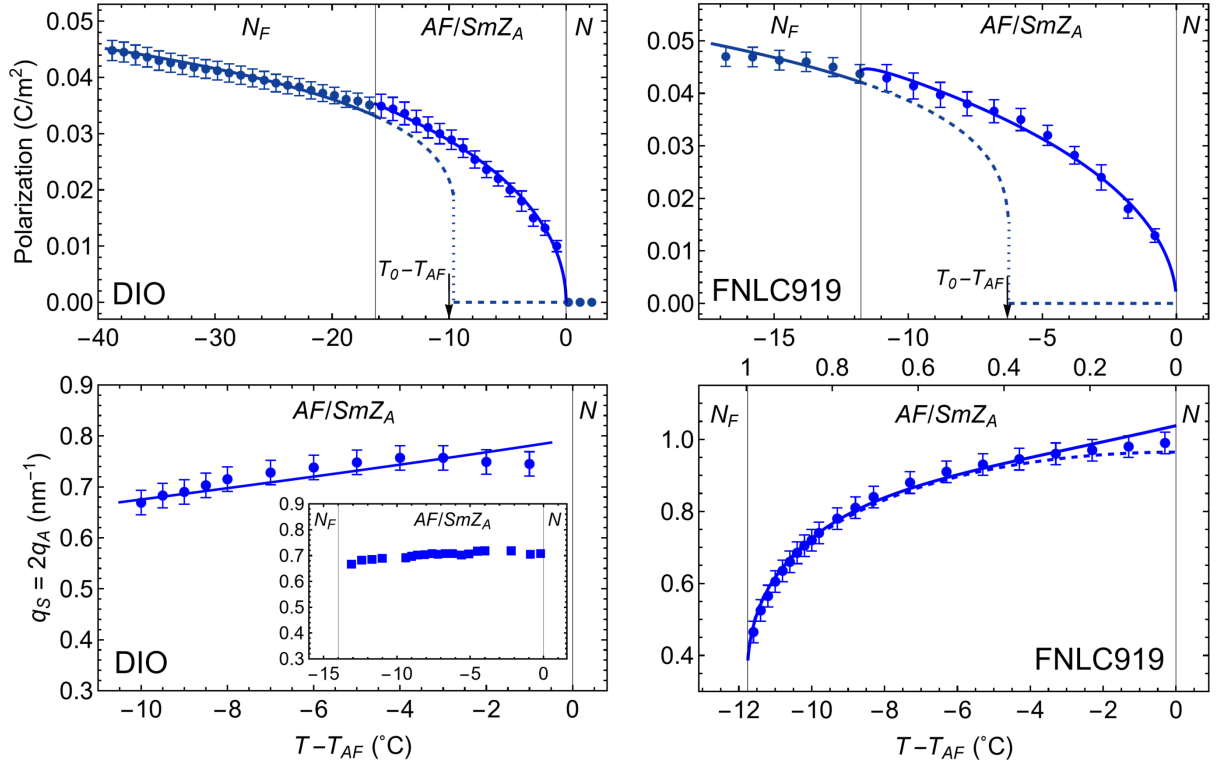


FIG. 2. Temperature dependence of the saturated polarization and wave number $q_s = 2q_A$ associated with the SmZ_A density modulation in *trans* DIO (left column) and FNLC919 (right column). Data for the antiferroelectric phase are distinguished by the lighter blue color. For comparison, the inset in the bottom left panel plots q_s data for DIO reported in Ref. [9] and reprinted with permission. Solid curves through the data for DIO are plots of Eqs. (3) and (4), using a single set of Landau parameters, in the limit of a purely sinusoidal polarization profile over the antiferroelectric range [see Eqs. (A4) and (A5)]. For FNLC919, the solid lines are plots of Eqs. (3) and (4), again for a single set of Landau parameters, in the case of polarization modulation that evolves from sinusoidal to solitonlike near the transition to the ferroelectric phase, where q_s decreases sharply. The dashed line on the q_s data is the quantity $1/K(k)$ in Eq. (3) multiplied by a constant scale factor. In the top panels, dashed/dotted lines extrapolate the polarization in the ferroelectric phase modeled by Eq. (4) through a “virtual” first-order ferroelectric to paraelectric nematic transition that would occur if the antiferroelectric phase was absent.

The temperature dependence of q_s for DIO and FNLC919 is plotted versus $T - T_{AF}$ in the bottom row of Fig. 2. In the case of DIO, the data only cover the upper 60% of the antiferroelectric range because diffraction from the density wave for $T - T_{AF} \lesssim -10^\circ\text{C}$ using our conventional x-ray source was too weak to identify the peak position. Over the observable range, the value of q_s decreases slightly with decreasing T . The synchrotron x-ray diffraction measurements on DIO in Ref. [9], reprinted with permission in the inset in Fig. 2, show a marginally weaker variation of q_s with T over nearly the complete range of the antiferroelectric phase. The median values in the inset and main figure are in good agreement.

In the case of FNLC919, q_s could be determined down to about 0.4°C above the antiferroelectric to ferroelectric transition ($T = T_F$). Closer to T_F , the peak merges into the edge of the undiffracted main beam, and there is no clearly defined local intensity maximum. The value of q_s decreases slowly through the upper antiferroelectric range and then drops sharply close to the transition, a behavior quite distinct from DIO. The value $q_s = 0.99\text{ nm}^{-1}$ just below the transition from the nematic phase is $\sim 30\%$ higher than in DIO and corresponds to a layer spacing $\Lambda_S = 6.3\text{ nm}$.

In order to observe diffraction from the weak smectic- Z_A density wave, relatively wide settings of the beam collimation

slits had to be used, which significantly degraded the peak-width resolution. Thus, the inverse FWHM obtained from the analysis of the peak profiles in Fig. 2 does not provide an accurate estimate of the correlated domain size. That said, within the lower third of the antiferroelectric phase in the FNLC919 sample, where q_s decreases more sharply, the peak broadens by about 50%, indicating diminishing smectic- Z_A layer correlations as $T \rightarrow T_F$.

The top row of Fig. 2 shows experimental results for the saturated polarization in the antiferroelectric and ferroelectric phases of DIO and FNLC919. With decreasing temperature, the polarization magnitude increases continuously through the antiferroelectric phase, crossing into the ferroelectric phase without a noticeable jump.

IV. DISCUSSION

Various theoretical approaches have been put forward to explain the occurrence of an antiferroelectric phase between the paraelectric and ferroelectric nematic phases. One approach [21,22,32–36] focuses explicitly on the coupling of polar interactions with elastic deformations of the director field. It describes the antiferroelectric ordering by filling space with splayed polar domains that reverse polarization direction

periodically along one or two directions (normal to the average director). The splay modulation is stabilized by a balance of Frank elastic energy, flexoelectric coupling between director splay and polarization $\vec{P}$, electrostatic energy incurred by accumulation of bound charge in the splayed domains, Landau terms in P^2 that favor a spontaneous polarization below a characteristic temperature, and gradient terms in $\vec{P}$. A “minimal” model of the free-energy density, given by Kats [22], anticipated the possibility of a stable modulated (antiferroelectric) phase between uniform paraelectric and ferroelectric nematic phases. In the simplest splay-based models, the modulation period Λ_A is set by competition between the intrinsic splay curvature (determined by the flexoelectric coupling constant, splay elastic constant, and polarization amplitude) and the electrostatic energy incurred by the accumulation of bound charge due to the polarization splay.

The electrostatic energy depends strongly on the number density n_q and charge q of ions (present as impurities or added as dopants) that effectively screen the bare Coulomb potential beyond the Debye length, $\lambda_D = \sqrt{\epsilon\epsilon_0 k_B T / (2q^2 n_q)}$. After doping with a miscible ionic fluid (thereby reducing λ_D), certain ferroelectric nematics exhibit optical stripe patterns, consistent with a splay modulation, over a temperature range between the paraelectric and ferroelectric nematic phases [35]. The modulation period is in the micron range, in agreement with calculations based on a model in which domains of opposite polarization splay (but constant $|\vec{P}|$) are separated by well-defined domain walls across which the direction of $\vec{P}$ reverses. Both Λ_A and the calculated width of the walls, d_w , significantly exceed the Debye length over the range of the antiferroelectric phase and over at least an order of magnitude change in λ_D —i.e., $\lambda_D \ll d_w < \Lambda_A$.

In contrast to the ion-doped ferronematic materials, the period of polarization modulation in the undoped DIO and FNLC919 samples studied in the present work is on the nanometer scale, $\Lambda_A = 2\pi/q_A = 4\pi/q_S \sim 10$ –20 nm. In this case, if $\lambda_D \gg \Lambda_A$, the electrostatic energy cost due to the bare Coulomb potential strongly suppresses polarization splay over lengths $\sim \Lambda_A$. To estimate λ_D for the DIO and FNLC919 samples studied, their ionic content was measured in the nonpolar N phase; details are given in the Supplemental Material [40]. The results are $n_q \approx 1.0 \times 10^{21} \text{ e/m}^3$ for DIO and $1.3 \times 10^{21} \text{ e/m}^3$ for FNLC919 at $T - T_{AF} = 40^\circ\text{C}$ and 20°C , respectively. Taking $q = e$ and $\epsilon = \epsilon_\perp = 50$, and accounting for uncertainties in the values of n_q , give $\lambda_D \approx 220 (\pm 5\%) \text{ nm}$ for the DIO and $170 (\pm 7.7\%) \text{ nm}$ for the FNLC919 samples. These values are ~ 10 times larger than the respective values of Λ_A determined from the data for q_S and imply $\lambda_D \gg d_w$, opposite of the result obtained from the splay-modulated model applied to ion-doped ferroelectric nematics for a large range of n_q .

Chen *et al.* [9] and co-workers [37] considered an alternative model of the antiferroelectric order for the case where ionic screening of polarization charge is weak, and polarization splay is expelled due to high electrostatic energy cost. The director $\hat{n}$ is essentially uniform, while the amplitude P of the polarization $\vec{P} = P\hat{n}$ passes through zero and reverses sign periodically across Ising walls. In this so-called “pure polarization reversal” (PPR) model, a weak mass density modulation is produced by slightly closer packing

between molecules in the polarized domains relative to the domain walls where the polarization passes through zero. The smecticlike density wave is therefore a consequence of the antiferroelectric polarization modulation. (The same mechanism also applies in the splay-modulated models, where the domain walls are also Ising type.)

To develop an analytic framework for the PPR model incorporating the paraelectric/antiferroelectric/ferroelectric sequence of phase transitions, Chen *et al.* insightfully drew a connection to the well-established Landau theory that describes analogous phenomena in solid ferroelectrics [27–30]. They successfully used the theory to explain both the stabilization of the antiferroelectric/smectic- Z_A phase by long-range dipolar interactions and the weak temperature dependence of the wave number $q_S = 2q_A$ in DIO that follows when the modulation of P is nearly sinusoidal.

The remainder of this section demonstrates that the Landau theory invoked by Chen *et al.* can be used to analyze quantitatively the results in Fig. 2 for the key equilibrium parameters—polarization magnitude and wave number—that characterize the antiferroelectric phase in both DIO and FNLC919, where the experimental temperature dependencies of q_S are quite distinct. The equilibrium free-energy density is expanded in even powers of P and its derivatives along a direction $\hat{x}$ normal to the (fixed) polarization axis ($\hat{z}$) as

$$f = \frac{a(T)}{2}P^2 + \frac{b}{4}P^4 + \frac{c}{6}P^6 + \frac{\alpha}{2}\left(\frac{dP}{dx}\right)^2 + \frac{\beta}{2}\left(\frac{d^2P}{dx^2}\right)^2 + \frac{\eta}{2}P^2\left(\frac{dP}{dx}\right)^2, \quad (1)$$

where $a(T) = a_0(T - T_0)$ and the coefficients a_0, c, β, η are positive and constant in T . If $\alpha < 0$ in Eq. (1), an antiferroelectric phase with $P = P(x)$ alternating along x may be stabilized between higher temperature paraelectric and lower temperature ferroelectric phases. For $\alpha > 0$, there is no stable antiferroelectric phase, and a direct, first (second) order paraelectric to ferroelectric transition occurs at $T = T_0 + 3b^2/16a_0c$ ($T = T_0$) if $b < 0$ ($b > 0$). The term in β in Eq. (1) stabilizes the antiferroelectric ordering at finite q_A . The term in η produces an explicit dependence of q_A on P [see Eqs. (A2) and (A4)].

Variation of the integrated f in Eq. (1) yields a nonlinear fourth order differential equation for P . As shown by Klepikov and Berezovsky [38] (see Appendix), approximate solutions are Jacobi elliptic functions, among which is the elliptic sine,

$$P = P_0 \text{sn}(lx, k) \equiv P_0 \text{sn}(u, k). \quad (2)$$

Here, P_0, l , and the modulus k ($0 \leq k < 1$) are variational parameters that minimize f averaged over the period Λ_A of the P profile, $\Lambda_A = 4K(k)/l$, where $K(k)$ is the complete elliptic integral of the first kind.

Equation (2) reduces to a simple sinusoid, $P = P_0 \sin(lx)$, when $k \rightarrow 0$, which is reasonable to expect close to a weakly first-order antiferroelectric to paraelectric transition. As $k \rightarrow 1$, the periodic profile becomes increasingly solitonlike, with the characteristic width of Ising walls between domains wherein $P \approx \pm P_0$ becoming a smaller fraction of the spatial period. This behavior may be expected close to the ferroelectric phase. The period Λ_A reduces to $2\pi/l$ at $k = 0$ and

diverges as $k \rightarrow 1$ [due to the divergence of $K(k)$], which implies a strong decrease in the wave numbers q_A and q_S , given by

$$q_S = 2q_A = \frac{4\pi}{\Lambda_A} = \frac{\pi l}{K(k)}. \quad (3)$$

Such a decrease is observed in the results for q_S at lower temperatures in the antiferroelectric phase of FNLC919 (Fig. 2) and, according to the model, signals the development of a solitonlike modulation.

The (k, T) dependence of l and P_0 may be obtained by inserting Eq. (2) into Eq. (1), averaging over x , and minimizing the average free-energy density $\bar{f}$ over l and P_0 . The result for l is given by Eq. (A2). For P_0 , one obtains

$$P_0^2(k, T) = -\frac{B(k)}{2C(k)} + \sqrt{\frac{B(k)^2}{4C(k)^2} - \frac{A(k, T)}{C(k)}}. \quad (4)$$

In the antiferroelectric phase, the quantities $A(k, T)$, $B(k)$, and $C(k)$ are expressed [Eq. (A3)] in terms of the Landau coefficients $a(T)$, b , c , α , β , η , and u -averaged combinations of $\text{sn}(u, k)$ and its derivatives with respect to u . Stability of the antiferroelectric phase requires $C(k) > 0$. The nematic to antiferroelectric transition occurs for $\alpha < 0$ at the temperature (T_{AF}) , where $A(k, T) = 0$. If $k \rightarrow 0$ as $T \rightarrow T_{AF}$ from below (pure sinusoidal polarization modulation at the paraelectric to antiferroelectric transition), this condition gives $T_{AF} = T_0 + \frac{\alpha^2}{4\beta a_0}$.

In the ferroelectric phase, P is uniform in space and $A(k, T) \rightarrow a(T)$, $B(k) \rightarrow b$, and $C(k) \rightarrow c$ in Eq. (4). The transition from the antiferroelectric to ferroelectric phase happens at the temperature (T_F) , where the value of $\bar{f}$ for the two phases is the same.

The weak T dependence of $q_S = 2q_A$ in DIO implies that $K(k)$ in Eq. (3) does not vary significantly over the antiferroelectric range. One may then consider simplifying the model by taking the small k limit, where Eq. (2) reduces to $P = P_0 \sin(q_A x)$ and $K(k \rightarrow 0) \rightarrow \pi/2$.

The solid lines in Fig. 2 through the data points for saturated polarization and q_S in DIO are calculated from the $k \rightarrow 0$ limits of Eqs. (3) and (4), using a *single* set of reduced Landau coefficients for both the antiferroelectric and ferroelectric phases. Their values are $\frac{b}{a_0} = -4.36 \times 10^3 \text{ m}^4 \text{ K/C}^2$, $\frac{c}{a_0} = 9.21 \times 10^6 \text{ m}^8 \text{ K/C}^4$, $\frac{\alpha}{a_0} = -1.27 \times 10^{-16} \text{ m}^2 \text{ K}$, $\frac{\beta}{a_0} = 4.04 \times 10^{-34} \text{ m}^4 \text{ K}$, and $\frac{\eta}{a_0} = 1.69 \times 10^{-13} \text{ m}^6 \text{ K/C}^2$, with $T_0 - T_{AF} = -10^\circ \text{C}$.

These values are constrained by the following conditions: (1) $T_0 - T_{AF} = -\frac{\alpha^2}{4\beta a_0}$; (2) $\bar{f}_{AF}(T_F) = \bar{f}_F(T_F)$ (the average free-energy densities of the ferroelectric and antiferroelectric phases are equal at the transition $T = T_F$); (3) the amplitude of the modulated antiferroelectric polarization should be comparable to (or less than) the ferroelectric polarization at T_F ; and (4) $T_F < T_0 < T_{AF}$. As a result of these conditions, only four parameters in the above list may be freely varied. In the polarization measurement, T_{AF} and T_F were determined from the onset of antiferroelectric switching and the crossover from antiferroelectric to ferroelectric switching, respectively. In the SAXS data, the initial detection of the density modulation on cooling was used to fix T_{AF} (within $\sim 0.5^\circ \text{C}$). Figure 3

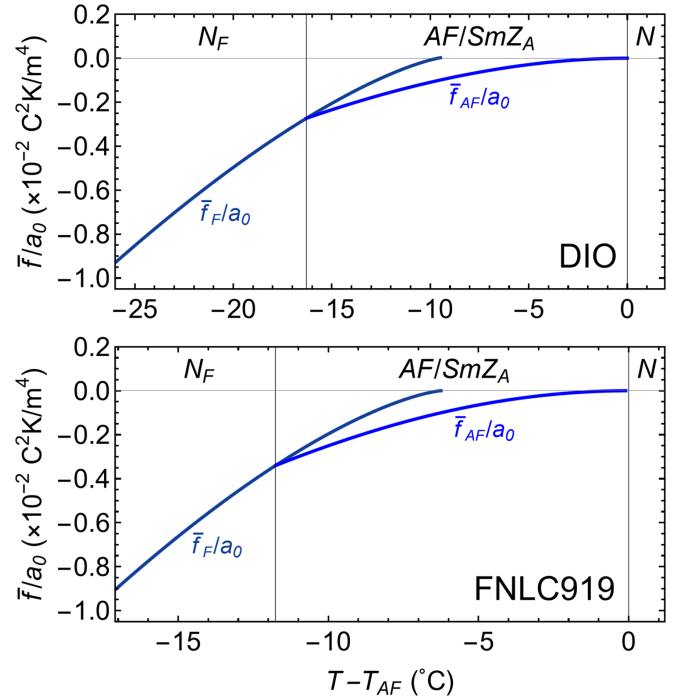


FIG. 3. Average free-energy densities (divided by a_0) calculated in the ferroelectric and antiferroelectric phases of DIO (top panel) and FNLC919 (bottom panel) from the model in Eqs. (1) and (2), the expressions for q_A and P_0 given in Eqs. (3), (4), and (A2)–(A5), and the values of reduced Landau coefficients and T_0 used to model the data in Fig. 2. The energies are equal at $T - T_{AF} = -16.3^\circ \text{C}$ for DIO and $T - T_{AF} = -11.8^\circ \text{C}$ for FNLC919 (indicated by vertical lines).

confirms that the condition $\bar{f}_{AF}(T_F) = \bar{f}_F(T_F)$ is satisfied for the parameters used to model the data in Fig. 2 for DIO. The vertical line in the figure corresponds to $T_F - T_{AF} = -16.3^\circ \text{C}$, which matches the experimentally determined value from the polarization data.

In contrast to the analysis for DIO, the k dependence in Eq. (3) becomes important to describe the behavior of q_S in FNLC919—specifically, its sharp pretransitional downturn as $T \rightarrow T_F$. The dashed curve through the q_S data points for FNLC919 (Fig. 2) is a plot of $1/K(k)$ on a linear scale in k (top axis in the figure) multiplied by a constant factor to match the data, which are plotted on a linear scale in T (bottom axis). The comparison suggests the linear function $k(T) = k_0(T_{AF} - T)$ is a reasonable first-order approximation for the T dependence of k over the measured range of q_S .

The solid lines plotted on the data for FNLC919 in Fig. 2 are calculated from Eqs. (3) and (4) using the set of reduced Landau coefficients $\frac{b}{a_0} = -6.78 \times 10^2 \text{ m}^4 \text{ K/C}^2$, $\frac{c}{a_0} = 2.12 \times 10^6 \text{ m}^8 \text{ K/C}^4$, $\frac{\alpha}{a_0} = -4.68 \times 10^{-17} \text{ m}^2 \text{ K}$, $\frac{\beta}{a_0} = 8.68 \times 10^{-35} \text{ m}^4 \text{ K}$, and $\frac{\eta}{a_0} = 3.80 \times 10^{-14} \text{ m}^6 \text{ K/C}^2$, and the linear form for $k(T)$, with $k_0 = 0.0848$. The value of $T_0 - T_{AF}$ is -6.3°C . Again, only four of Landau parameters, plus k_0 , are varied freely. At the lower end of the data plotted for q_S , the modulus $k = 0.98$, which from Eq. (2) implies a solitonlike polarization profile at low temperature in the

antiferroelectric phase of FNLC919. Despite deviations from the data for q_S at higher T and in the slope of P in the N_F phase, the agreement between the model and experimental results is fairly good.

For the parameter values listed above, the plots of $\bar{f}_{AF}$ and $\bar{f}_F$ in Fig. 3 give $T_F - T_{AF} = -11.8^\circ\text{C}$ in FNLC919. This value, obtained from the modeling and shown by the vertical lines in the right panels of Fig. 2, is still $\sim 0.2^\circ\text{C}$ above the temperature at which the smectic- Z_A diffraction peak fully disappeared into the shoulder of the undiffracted beam. The discrepancy may reflect inaccuracy in the assumption of a linear variation of k , with T or possibly a narrow coexistence region due to the multicomponent composition of FNLC919. Higher-resolution SAXS data close to T_F and a proper calculation of the temperature dependence of k —i.e., by minimizing $\bar{f}$ over k and then solving the resulting transcendental equation to find the value of k at each T for a given set of Landau coefficients—would enable a better test of the model for q_S close to T_F , as well as possibly improving its description of the data near T_{AF} . One could also consider retaining powers of P in Eq. (A1) beyond P^4 , which would result in more complicated, hyperelliptic functions as solutions for the spatial profile of P [39].

It is interesting that the model for the amplitude of the polarization modulation [Eq. (4)] accurately represents the saturated polarization under applied electric field in the antiferroelectric phase of both materials studied. This suggests that under an applied field sufficient to saturate the polarization current, the polarization switches between oppositely polarized states with $|\bar{P}| \simeq P_0$ (the amplitude of the modulation in the ground state).

As a final point, detection of higher harmonics of the smectic- Z_A layer structure by SAXS as $T \rightarrow T_F$ in FNLC919 would provide a more direct experimental indication of a developing solitonlike polarization modulation. However, this would be challenging for three reasons: very weak intrinsic scattering from the first harmonic, lower relative amplitudes of the higher harmonics (even approaching a strongly solitonlike profile), and suppression of the higher harmonic intensities by thermal fluctuations of the smectic- Z_A layers. As described in Sec. S4 of the Supplemental Material [40], calculations using the model in Eq. (2) confirm that the second harmonic is too weak to observe in the SAXS measurements reported here.

V. SUMMARY

To summarize, the magnitude and the wave number of the polarization field characterizing the antiferroelectric/smectic- Z_A phase of two ferroelectric nematic liquid crystals were compared quantitatively, and overall favorably, to a Landau theory originally developed to describe antiferroelectric ordering in solid ferroelectrics. The comparison to theory indicates that the spatial profile of the modulation evolves rather differently with temperature in the two liquid crystals studied. In the compound DIO, the modulation maintains an essentially sinusoidal (single harmonic) profile deep into the antiferroelectric phase, whereas in the commercial mixture FNLC919 a sharp decrease in the modulation wave number indicates development of a significantly solitonlike polarization profile on approach to the antiferroelectric to ferroelectric transition.

The present work also demonstrates that diffraction from the very weak mass density wave accompanying the polarization modulation in the antiferroelectric phase of ferroelectric nematics can be detected with conventional laboratory SAXS instrumentation.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX: FURTHER DETAILS ON APPROXIMATE SOLUTION OF THE MODEL PRESENTED IN EQ. (1)

The physically relevant solutions of the differential equation obtained from $\delta(\int d\bar{r}f) = 0$ are periodic in x and can be expressed as a Fourier series, $P(x) = \sum_n P_n \sin[(2n+1)q_A x]$, with the even harmonics excluded since P alternates ($P \rightarrow -P$) in each half-period in the antiferroelectric phase—i.e., $P(x + \Lambda_A/2) = P(x + \pi/q_A) = -P(x)$. The amplitudes P_n and wave number q_A are variational parameters that depend on T and are determined by minimizing the average free-energy density $\bar{f}$ over one period.

Klepikov and Berezovsky [38] demonstrated that the solutions also satisfy the following nonlinear equation for the first derivative of P :

$$\left(\frac{dP}{dx}\right)^2 = \sum_{n=0}^{\infty} A_{2n} P^{2n} = A_0 + A_2 P^2 + A_4 P^4 + \dots \quad (\text{A1})$$

The coefficients A_{2n} are another set of variational parameters whose values minimize $\bar{f}$.

Limiting the number of terms in the sum on the right-hand side of Eq. (A1) leads to approximations for the polarization profile that are more physically realistic than truncating the Fourier series (which would produce a profile with unphysical ripples due to limiting the number of spatial frequencies). The Jacobi sine function [Eq. (2)] is a solution for terms up through P^4 . If higher powers of P are retained the solutions are more complicated, hyperelliptic functions. The variational parameters P_0 , l , and the modulus k in Eq. (2) are related to A_0 , A_2 , and A_4 by $A_0 = P_0^2 l^2$, $A_2 = -l^2(k^2 + 1)$, and $A_4 = l^2 k^2 / P_0^2$.

Minimizing $\bar{f}$ over parameter l in the approximate solution [Eq. (2)] gives

$$l^2 = -\frac{\alpha}{2\beta} \frac{\overline{\text{sn}^2(u, k)}}{\overline{\text{sn}''^2(u, k)}} - \frac{\eta P_0^2}{2\beta} \frac{\overline{\text{sn}^2(u, k) \text{sn}^2(u, k)}}{\overline{\text{sn}''^2(u, k)}}, \quad (\text{A2})$$

where primes indicate derivatives with respect to the variable u and the averages $\overline{(\cdots)}$ are computed as $\overline{(\cdots)} = \frac{1}{4K(k)} \int_0^{4K(k)} (\cdots) du$. Their ratios depend only weakly on modulus k . Note that with $(\beta, \eta) > 0$, l is real valued only if $\alpha < 0$. (A requirement for existence of an antiferroelectric phase.)

The explicit forms of the averages in Eq. (A2) are

$$\begin{aligned} \overline{\text{sn}^2(u, k)} &= \frac{K(k) - E(k)}{k^2 K(k)}, \\ \overline{\text{sn}^4(u, k)} &= \frac{(2 + k^2)K(k) - 2(1 + k^2)E(k)}{3k^4 K(k)}, \\ \overline{\text{sn}^6(u, k)} &= \frac{(8 + 3k^2 + 4k^4)K(k) - (8 + 7k^2 + 8k^4)E(k)}{15k^6 K(k)}, \\ \overline{\text{sn}^2(u, k)} &= \frac{(1 + k^2)E(k) - (1 - k^2)K(k)}{3k^2 K(k)}, \\ \overline{\text{sn}''^2(u, k)} &= \frac{(7 - 18k^2 + 11k^4)K(k) - (7 - 22k^2 + 7k^4)E(k)}{15k^2 K(k)}, \\ \overline{\text{sn}^2(u, k) \text{sn}''^2(u, k)} &= \frac{2(1 - k^2 + k^4)E(k) - (2 - 3k^2 + k^4)K(k)}{15k^4 K(k)}, \end{aligned}$$

where $K(k)$ and $E(k)$ are complete elliptic integrals of the first and second kind, respectively.

The amplitude P_0 of the polarization modulation appearing in Eq. (A2) is given by Eq. (4) with

$$\begin{aligned} A(k, T) &= a_0(T - T_0) \overline{\text{sn}^2(u, k)} - \frac{\alpha^2}{4\beta} \frac{(\overline{\text{sn}^2(u, k)})^2}{\overline{\text{sn}''^2(u, k)}}, \\ B(k) &= b \overline{\text{sn}^4(u, k)} - \frac{\eta\alpha}{\beta} \frac{\overline{\text{sn}^2(u, k) \text{sn}^2(u, k)} \overline{\text{sn}^2(u, k)}}{\overline{\text{sn}''^2(u, k)}}, \\ C(k) &= c \overline{\text{sn}^6(u, k)} - \frac{3\eta^2}{4\beta} \frac{(\overline{\text{sn}^2(u, k) \text{sn}^2(u, k)})^2}{\overline{\text{sn}''^2(u, k)}}. \quad (\text{A3}) \end{aligned}$$

One could combine all of the above with Eqs. (1)–(4) and then minimize $\bar{f}$ over k to obtain a complicated transcendental equation for the temperature dependence of the modulus k . A numerical analysis of the result could be used potentially to improve the modeling of the data for FNLC919 in Fig. 2.

In the $k = 0$ limit (pure sinusoidal polarization profile), Eqs. (3) and (4) reduce to

$$\begin{aligned} q_S(T) &= 2q_A(T) = \sqrt{-\frac{2\alpha}{\beta} - \frac{\eta P_{0,AF}^2(T)}{2\beta}}, \quad (\text{A4}) \\ P_{0,AF}^2(T) &= -\frac{3b - \frac{\eta\alpha}{\beta}}{5c - \frac{3\eta^2}{8\beta}} \\ &\quad + \sqrt{\left(\frac{3b - \frac{\eta\alpha}{\beta}}{5c - \frac{3\eta^2}{8\beta}}\right)^2 + \frac{8a_0(T_{AF} - T)}{5c - \frac{3\eta^2}{8\beta}}}, \quad (\text{A5}) \end{aligned}$$

in the antiferroelectric phase, with $T_{AF} = T_0 + \frac{\alpha^2}{4\beta a_0}$. These expressions were used in the analysis of the data for DIO in Fig. 2.

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