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Ground-state phase diagram of a one-dimensional discotic liquid crystal in a local anisotropy field

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The ground-state phases of a chiral model which describes orientational order of a single stack of planar objects with threefold symmetry subject to a local anisotropy field are examined. The results are used to interpret experimental data on columnar discotic liquid crystals which exhibit triangular arrays of helically ordered molecular stacks.

I. INTRODUCTION

Discotic mesophases having a regular two-dimensional arrangement of parallel columns of disklike molecules are now known to exist.[1,2] Such states are realizations of two-dimensional long-range positional order (rectangular or triangular) in a three-dimensional solid.[3] In this idealized view of columnar liquid crystals, the intracolumn behavior is liquidlike and in the absence of defects, the columns glide freely over each other.[4] The mechanical properties of a model which excludes shear strain acting along the columns leads to both buckling and undulation instabilites.[5] These features were observed experimentally[6] in a particular discotic liquid crystal composed of hexa-*n*-octyloxytriphenylene molecules (HET) indicating, however, the presence of an anomalously large (for a liquid crystal phase) column curvature elastic constant. More recent depolarized Rayleigh scattering experiments[7] suggested that the column undulation is not controlled by curvature elasticity but by extrinsic solidlike three-dimensional elastic behavior due to column entanglements or defects. This interpretation has been challenged by Brand and Pleiner[8] who maintain that the liquid crystal phase studied in Ref. 7 has true three-dimensional long-range positional ordering due to intercolumn correlations.

The structural properties of a related compound composed of hexa-hexylthiotriphenylene molecules with D_3 symmetry (HHTT) have been examined in some detail by x-ray diffraction[9–11] and are most relevant to the present study. Discotic columnar mesophases exist in this material at temperatures $T < 93\,^\circ\mathrm{C}$ with the columns forming a triangular array. At lower temperatures, $T < 70\,^\circ\mathrm{C}$, helical ordering along the stacking axis is observed. This order is accompanied by a period-three basal-plane superlattice structure associated with one-third of the columns having a vertical displacement. The relative chirality of the columns also has a period-three structure; however, further characterization of this quantity appears to be dependent on experimental conditions. Indeed, the initial x-ray data on oriented strands of HHTT (Ref. 9) were interpreted as resulting from an incommensurate helical order along the columns with an intermolecular rotation angle of 45.5°. This study also concluded that the undisplaced stacks had the same chirality while the displaced stacks had a random chirality implying no long-range order. A subsequent study[10] reported that a better fit to the x-ray results were obtained by assuming the displaced stack had helical order with a chirality opposite to that of the undisplaced columns.

More recent high resolution powder diffraction results[11] on the same material were used to study the phase diagram of hexa-*n*-alkylthiotriphenylenes as a function of the length n of the six chains surrounding the triphenylene core. In these bulk materials, for an effective n ranging from 5.65 to 6.10 carbons, a (three-dimensional) helically ordered discotic phase is observed with a commensurate periodicity involving eight molecules (45°). Their analysis suggests that the side chains form an isotropic oil surrounding the rigid cores. At the smaller and larger values of n for which this phase is stable, additional structure is observed corresponding to some columns having an incommensurate helical pitch of 47.2°. The presence of only incommensurate helical structure in the strand geometry was then interpreted as a consequence of a large surface tension.

The results discussed above[5–11] point to a set of unanswered questions and issues regarding helically ordered discotics. An important one being: To what extent does long-range helical order imply long-range three-dimensional positional order? Which may be rephrased: What freedom remains for the stacks to glide freely over each other in this phase? It also remains to be understood why there is such a strong dependence of the helical pitch on the geometry and sample constraints, even leading to the coexistence of commensurate and incommensurate structures under certain conditions. Common to all these features is the role played by the local environment of a single column. Although known to be weaker than the intracolumn couplings, these spatial-average intercolumn interactions can play an important role in the helical order of a single stack. The work reported here answers some of these questions and serves to compliment and extend other work in this field[12–14] as well as providing the basis for a more detailed treatment.

The remainder of this paper is organized as follows.

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In Sec. II, the model of a helical column in a sixfold or threefold anisotropy field is presented. Analytical and numerical results pertaining to the stability of the period-eight phase are given in Sec. III. Finally, a discussion of the results is made in Sec. IV with reference to the ground-state behavior of the helically ordered discotic.

II. THE MODEL

Figure 1 shows the two-dimensional pattern of the columns as proposed in Ref. 9 for HHTT in its helically ordered phase. Undisplaced stacks are shown by full circles and displaced stacks by open circles. At the lowest temperature at which this phase is stable, the relative interstack displacement approaches one-half of the intrastack intermolecular separation. Two types of two-dimensional local environments are then present which are due to the geometry of the surrounding stacks: the displaced and undisplaced stacks are in local anisotropy fields which are predominantly sixfold and threefold, respectively. We do not attempt to formulate a complete picture of these complex systems which involves cooperative states of all the stacks interacting together, but rather a simple model is considered which pertains to a single stack. We study the effect of the local anisotropy field on the helical pitch of a column in the belief that useful knowledge can be gained in the context of elucidating the role of competing periodicities.

The potential energy for the angular dependence of a single stack of molecules with D_3 symmetry (see Fig. 2) is then written as

$$E[\theta_n] = -J_0 \sum_n \cos 3(\theta_{n+1} - \theta_n - \alpha) - \tfrac{1}{2} H \sum_n \cos(p\theta_n) \ , \qquad (1)$$

where θ_n is the angular coordinate of the nth molecule with respect to a fixed direction perpendicular to the stacking axis,[13] J_0 is the nearest-neighbor intracolumn chiral interaction strength, H is the local angular anisotropy field of p-fold symmery, and α is a measure of the natural angle of rotation between a nearest-neighbor pair of molecules in their lowest energy state. For the nonhelical case ($\alpha = 0$), we have the trivial ferromagnetic chain. For α and H different from 0, it is the competition between the two interaction terms of (1) (the first term sets the natural pitch of the helix, while the anisotropy term defines prefered directions), that gives rise to commensurate and incommensurate phases in this model.[14] For a study of states at $T = 0$ with classical rotation degrees of freedom, kinetic energy terms may be neglected. It has also been assumed that the intermolecular distances remain fixed so that only rotational degrees of freedom contribute to the potential energy (1).

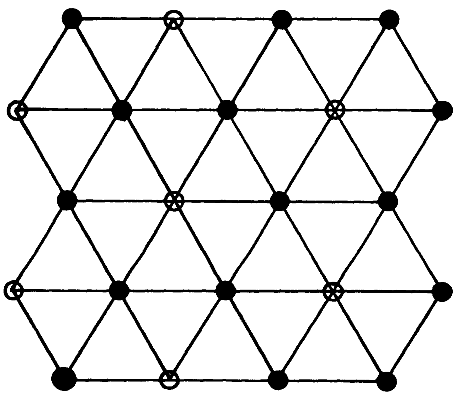

FIG. 1. The two-dimensional pattern of columns transverse to the stacking axis.

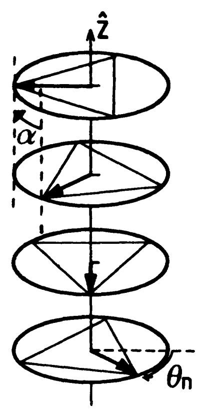

FIG. 2. Schematic sideview of a half-period in the 3/8 phase. The intermolecular turn angle is $\alpha = \pi/4$, so that a full period consists of eight molecules. However, because of the D_3 symmetry of the molecules (symbolized by triangles), one counts three full rotations of 2π over eight consecutive molecules.

With the change of variables $\phi_n = 3\theta_n$, the potential energy (1) reduces to that for a system of classical planar vectors with a chiral interaction in an anisotropy field of $p/3$ symmetry

$$E[\phi_n] = -J_0 \sum_n \cos(\phi_{n+1} - \phi_n - \Delta) - \tfrac{1}{2} H \sum_n \cos(p\phi_n/3) \ , \qquad (2)$$

where $\Delta = 3\alpha$. The main features of the $H - \Delta$ phase diagram for this model with $p = 3$ have been obtained by Yokoi *et al.*,[15] and for the case of a twofold anisotropy field ($p = 6$) by Banerjea and Taylor[16] and more recently by Hébert *et al.*[14] We examine here in detail the stability of the period-eight phase.

To specify the commensurate phases, we adopt the notation introduced by Yokoi *et al.*[15] The average nearest-neighbor intermolecular angle is written as

$$\langle \phi_{n+1} - \phi_n \rangle = 2\pi \bar{q} = q. \qquad (3)$$

A commensurate phase having P 2π rotations for the Q successive molecules of an entire period is specified using the rational number

$$\bar{q} = P/Q. \tag{4}$$

In the next section, we study analytically and numerically the region of stability in the $H - \Delta$ phase diagram of the 3/8 phase of the chiral vector model, i.e., three 2π rotations of the vectors for the eight successive sites of a given period. This state corresponds to a 45° intermolecular turn angle in the D_3-symmetry discotic model (see Fig. 2).

III. REGIONS OF STABILITY OF THE 3/8 PHASE

We first consider the case of the displaced stacks of the helical discotic, which are seen from Fig. 1 to be acted upon by a local anisotropy field of sixfold symmetry. This corresponds to an easy-axis anisotropy in the equivalent planar vector model with p=6. In the isotropic limit H=0 and with $\Delta = \Delta_c = 3(\pi/4)$, a commensurate 3/8 phase is stabilized.

For finite H, the otherwise freely rotating 3/8 phase is pinned to a particular orientation in the plane with concomitant angular distortions, as shown in Fig. 3 and discussed in the Appendix. This pinning allows the phase to occupy a finite region of the $H - \Delta$ phase diagram. An analytic formulation of the phase boundaries for the 3/8 phase based on the criteria of zero-energy creation for a single soliton (antisoliton) is presented in the Appendix. The presence of the anisotropy field fixes the global phase angle Φ to $\pi/8$ (see the Appendix). The phase boundaries at small H, as discussed in the Appendix, are given by

$$H = 12.6 \mid \tilde{\Delta}' \mid^{\frac{1}{2}} \tag{5}$$

for the soliton and

$$H = 3.68 \mid \tilde{\Delta}' \mid^{\frac{1}{2}} \tag{6}$$

for the antisoliton. The reduced chiral angle is given by $\tilde{\Delta}' = (\Delta - \Delta_c)/2\pi$ and H is measured in units of J_0. In both relations (5) and (6), $\tilde{\Delta}'$ is negative so that the domain of stability of the distorted 3/8 phase is located entirely in the region $\Delta < \Delta_c$, as shown in Fig. 4. The anisotropy field strongly pulls the 3/8 phase towards the symmetry point $\Delta = \pi/2$ of the easy-axis vector model. Thus in the case of a sixfold anisotropy field, the 3/8 phase is totally absent for $\Delta > 3\pi/4$.

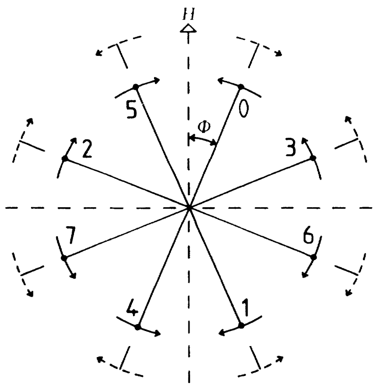

FIG. 3. Angular distortions of the 3/8 phase induced by the anisotropy field of sixfold symmetry. The meaning of the arrows is described in the text.

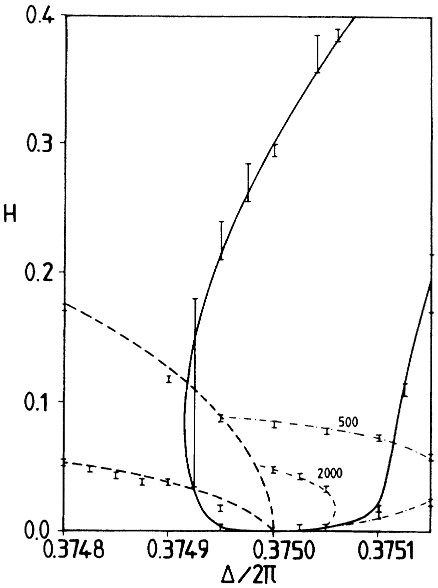

FIG. 4. Phase diagram for the 3/8 phase. Thick broken lines to the left for 0.3750 are analytic results obtained from (5) and (6) for the sixfold anisotropy field. Small vertical bars at low H indicate the phase-boundary region for this case as determined numerically. Good agreement is seen to the left of 0.3750. The region of stability of the 3/8 phase found to the right of 0.3750 only in the numerical results decreases with increasing ν, as indicated by the thin broken curves (guides to the eye) labeled 500 and 2000. The full curves (guides to the eye) with vertical bars correspond to the numerical results for the case of a threefold anisotropy field. The vertical bars represent portions of the H-scans where both 3/8 and higher-order commensurate phases were observed.

A numerical determination of the phase boundaries was also made using the effective potential method.[17] This technique has been used extensively in the recent literature; further details of our own implementation may be found in Ref. 14. Two quantities characterize the method; first, the number ν of equidistant points used to discretize the angular variables, and ε, an arbitrarily small parameter chosen to indicate that self-consistency has been achieved. Results for the region of stability of the 3/8 phase from the first calculation using ν=500 and $\varepsilon = 10^{-6}$ are shown in Fig. 4. Contrary to the analytic results, this first numerical approach leads to the appearance of a region of stability for $\tilde{\Delta}' > 0$. However, using ν=2000 and $\varepsilon = 10^{-7}$ yields a phase diagram with this discrepancy greatly reduced. The numerical results for $\tilde{\Delta}' < 0$ are in good agreement with expressions (5) and (6), as shown in Fig. 4. It appears likely that full agreement with the analytic results would occur if a very large value of ν and a very small ε were used.

Consider now the case of the undisplaced stacks which are subject to a threefold anisotropy field. For the vector model, this is equivalent to the presence of a magnetic field. The gross features of the phase diagram have been reported by Yokoi *et al.*[15] which show a symmetry point at $\Delta = \pi$ and a spin-wave-type instability from the 0/1 phase to the 1/2 phase for $H > 4$. Although there is evidence in this work that the domain of stability for the 3/8 phase rises nearly vertically (curving slightly to $\tilde{\Delta}' > 0$) a more accurate determination of the phase diagram at low H was made here. Efforts to employ the analytic approach discussed in the Appendix for this case proved fruitful only in the limit of very small H. To lowest order in $\tilde{\Delta}'$, the two boundary lines increase symmetrically as $H \sim |\tilde{\Delta}'|^{\frac{1}{4}}$. Results from a numerical determination of the phase boundary lines at higher H are also shown in Fig. 4. It opens up on both the positive and negative sides of $\tilde{\Delta}'$. For $\tilde{\Delta}' > 0$, the 3/8 phase persists up to $H \simeq 0.3$. At very small values of H, the boundaries are nearly flat followed by a rapid increase near $\tilde{\Delta}' \simeq 10^{-3}$.

IV. DISCUSSION AND CONCLUSIONS

The phase boundaries presented in Fig. 4 show clearly that the stability of a single column of D_3 molecules in an anisotropy field is strongly dependent on the symmetry of its local environment. As indicated in the Introduction, we may speculate that to a certain degree the structure of the stack will depend on the natural angle of rotation Δ (or α) and on the strength and symmetry of the surrounding field. Assuming that the natural angle of rotation for the HHTT molecules is 45° (i.e., $\Delta/2\pi = 0.3750$), our results suggest that the undisplaced columns will remain in the 3/8 phase for values $H \leq 0.3$. From the results indicated in Fig. 4 of Ref. 15, it can then be expected that transitions will occur to 1/3 and 1/2 phases at $H \simeq 2.4$ and 4.0, respectively (with the occurence of higher-order phases near these critical field values). In contrast, the displaced columns experience an anisotropy field which destabilizes the 3/8 phase even for infinitesimal values of H. According to Fig. 1 of Ref. 14, the stack would then be in an incommensurate or higher-order commensurate phase corresponding to an intermolecular turn angle larger than 45°. This result is of interest in view of the observation in HHTT of a structure with a periodicity of less than eight molecules,[9–11] as discussed in the Introduction.

The three-dimensional state is certainly a cooperative phase of all the columns and the effect of the intercolumn interaction is more than to produce a local anisotropy field. However, a rough model emerges from the results reported here where the undisplaced stacks are kept in the 3/8 commensurate state and the displaced stacks must accommodate this environment. Two situations may result from these constraints. First, the displaced stack is forced to also be in a type of 3/8 phase where this is achieved only on the average, with regions of discommensurations separating higher-order phases. The second scenario is that the displaced stack is in an incommensurate phase. This latter possibility would allow for the displaced columns to glide freely along the stacking axis. The sum of these possibilities is of interest in view of the variety of experimental results discussed in the Introduction, in particular, the absence of shear stress between the columns and the presence of defects in the stacks. Viscoelastic measurements at finite frequency are clearly of interest in order to examine in more detail the nature of the elastic interactions between columns. Finally we note that the predicted distortions of the 3/8 phase may be observable in scattering experiments as higher harmonics of the principal wave vector, provided that the thermal fluctuations associated with these weaker-intensity peaks are not large.

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APPENDIX

The purpose of this calculation[15] is to determine the phase boundaries of the distorted 3/8 phase in a sixfold anisotropy field at small values of H and Δ' (with $J_0 \equiv 1$), given by

$$\Delta' \;=\; \Delta - 3\pi/4. \tag{A1}$$

Assuming a distorted structure of period eight, the angular coordinates ϕ_n for finite H are written as

$$\phi_n \;=\; n(3\pi/4) + \xi_n + \Phi. \tag{A2}$$

For H=0, the distortions ξ_n are zero and the global phase angle Φ is undetermined. For $H > 0$, the ξ_n are expressed by

$$\xi_n \;=\; \sum_{0<q<\pi} A_q \cos(qn + \alpha_q) \;, \tag{A3}$$

where the wave number q is limited by the periodic boundary conditions of the full stack of N molecules and to values compatible with the period of eight molecules. The distortions having, respectively, one, two, three, and four periods inside the eight sites are written as

$$\begin{aligned} \xi_n \;=\; & t\cos(\pi n/4) + w\sin(\pi n/4) + u\cos(\pi n/2) \\ & + v\sin(\pi n/2) + y\cos(3\pi n/4) \\ & + z\sin(3\pi n/4) + (-1)^n x. \end{aligned} \tag{A4}$$

Using (A2) and this expression in the potential energy (2) expanded to fourth order in Δ' and H, one finds that the following amplitudes minimize the energy:

$$u \;=\; a\sin(2\Phi) + b\sin^3(2\Phi) \;, \tag{A5}$$

$$v \;=\; -a\cos(2\Phi) - b\cos^3(2\Phi) \;, \tag{A6}$$

$$x \;=\; c\sin(4\Phi) \;, \tag{A7}$$

where

$$a = -\tfrac{1}{2}H - \tfrac{1}{4}H\Delta'^2 - \tfrac{5}{16}H^3 , \tag{A8}$$

$$b = \tfrac{13}{24}H^3 , \tag{A9}$$

$$c = \tfrac{1}{8}H^2 + \tfrac{1}{16}H^2\Delta'. \tag{A10}$$

To this low order in H, the amplitudes t, w, y, and z are zero since they are associated with an odd number of periods inside the overall periodicity of eight. Substituting (A5)–(A10) into the expression for the potential energy yields the following lowest-order Φ-dependent term:

$$\Delta E = -\tfrac{17}{48}H^4\sin^2(4\Phi). \tag{A11}$$

This result demonstrates that the global phase angle is pinned at $\Phi = \pi/8$ by the field H. Figure 3 shows schematically the distortions of the period-eight phase. The inner full arrows indicate the directions of the rotational distortions of period-two while the outer broken arrows show the same property for the period-four distortions.

It is now assumed that the distorted 3/8 phase is rendered unstable by the spontaneous appearance of solitons. The defect we consider corresponds to a slow variation of the phase angle Φ along the stack with an overall change of $\pm\pi/4$. The solitons are taken to have a mutual repulsive energy and as a consequence the zero of the single soliton creation energy identifies the limits of stability of the 3/8 phase. Treating the position along the stack n as a continuous variable, and using the results (A5)–(A10), the potential energy relative to the distorted 3/8 phase is

$$\begin{aligned}\epsilon = &-\left(\Delta' + \tfrac{1}{4}H^2 - \tfrac{1}{6}\Delta'^3 - \tfrac{1}{8}\Delta' H^2\right)[\Phi(\infty) - \Phi(-\infty)] \\ &+ \int_{-\infty}^{\infty} dn \left[\tfrac{1}{2}\left(\frac{d\Phi(n)}{dn}\right)^2 + \tfrac{7}{128}H^4\cos^2[4\Phi(n)]\right].\end{aligned} \tag{A12}$$

Solving the differential equation obtained from the extremal condition of this energy functional, with boundary conditions $\Phi(\pm\infty) = \pi/8$ or $3\pi/8$, the following soliton (+) or antisoliton (−), centered at $n = 0$, is obtained

$$\Phi(n) = \tfrac{1}{8}\pi + \tfrac{1}{2}\tan^{-1}\left\{\exp\left[\pm\tfrac{1}{2}\sqrt{7}H^2 n\right]\right\}. \tag{A13}$$

The energy of these solutions is

$$\begin{aligned}\epsilon = &-\left(\Delta' + \tfrac{1}{4}H^2 - \tfrac{1}{6}\Delta'^3 - \tfrac{1}{8}\Delta' H^2\right)[\Phi(\infty) - \Phi(-\infty)] \\ &+ \tfrac{1}{16}\sqrt{7}H^2.\end{aligned} \tag{A14}$$

For the (+) soliton, the boundary conditions are $\Phi(-\infty) = \pi/8$ and $\Phi(\infty) = 3\pi/8$. The zero of the creation energy is then given by (5), with $\tilde{\Delta}' < 0$. The antisoliton (−) has the boundary conditions $\Phi(-\infty) = 3\pi/8$ and $\Phi(\infty) = \pi/8$, with the zero of the creation energy given by (6), also with $\tilde{\Delta}' < 0$.

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