Transition to ordered intercalated columns in columnar liquid crystals

Jean-Guy Demers and Alain Caillé
Département de Physique, Université de Montréal, Case Postale 6128, Succursale Centre-ville, Montréal Québec, Canada H3C 3J7

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A phenomenological description of the phase transition between the disordered columnar phase D_{hd} and the ordered phase D_{ho} is presented in which the columns are ordered and displaced so as to relieve the intrinsic frustration on a triangular lattice. A number of additional phases are predicted, including the one observed experimentally for the hexa-hexylthiotriphenylene columnar liquid crystal.

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Columnar liquid crystal phases were first anticipated [1] and then observed [2]. The phase D_{hd} is a two-dimensional triangular lattice ordering of disordered columns. Hexa-hexylthiotriphenylene (HHTT), a molecule made of a rigid core with six hydrocarbon chains attached to it, has been observed for $70<T<93\,^{\circ}\mathrm{C}$ in the D_{hd} phase. On lowering the temperature, a transition to an ordered phase D_{ho} is observed. In the D_{ho} phase, a three-column superlattice structure sets in, with ordering along the columns of both the positional and orientational degrees of freedom and an intercalation between the columns. Using a phenomenological Landau approach, we investigate in this Brief Report the $D_{hd}\leftrightarrow D_{ho}$ transition, invoking only the positional degrees of freedom. Previous work has focused on transitions from the D_{hd} phase to a different two-dimensional phase [3], or involved an in-column ordering without the superlattice structure or assuming a uniform columnar modulation [4]. Experimentally, the $D_{hd}\leftrightarrow D_{ho}$ transition was studied by means of high-resolution x rays [5,6] and is known to also involve the orientational degrees of freedom, a situation which will be considered in an upcoming paper on the subject.

Without long-range order along the columns, the high-temperature symmetry group G_0 is not one of the classified 230 crystallographic space groups [7], but can be identified [8] as $(R\otimes Z^2)\wedge D_{6h}$. The point group D_{6h} for invertible hexagons is of order 24, and comprises a total of 12 classes. Primitive direct and reciprocal vectors describing the in-plane ordering of the D_{hd} phase may be chosen as

$$\mathbf{b}_1=a\hat{\mathbf{e}}_\mathbf{x},\quad \mathbf{b}_2=\frac{a}{2}\hat{\mathbf{e}}_\mathbf{x}+\frac{\sqrt{3}}{2}a\hat{\mathbf{e}}_\mathbf{y},$$

$$\mathbf{B}_1=\frac{2\pi}{a}\left(\hat{\mathbf{e}}_\mathbf{x}-\frac{1}{\sqrt{3}}\hat{\mathbf{e}}_\mathbf{y}\right),\quad \mathbf{B}_2=\frac{4\pi}{\sqrt{3}a}\hat{\mathbf{e}}_\mathbf{y}, \tag{1}$$

where a is the distance between adjacent sites. The lowest-harmonics expansion of molecular density is

$$\rho_0(\mathbf{x})=c_0+c_1\sum_{i=1}^{3}\cos(\mathbf{K}_i\cdot\mathbf{x}) \tag{2}$$

with the reciprocal vectors $\mathbf{K}_i\in\{\mathbf{B}_1,\mathbf{B}_2,-(\mathbf{B}_1+\mathbf{B}_2)\}$ and c_0 and c_1 two constants. The resulting triangular lattice is depicted in the contour plot of Fig. 1.

For a second-order or weakly first-order transition, the electronic density near the transition point takes the form $\rho(\mathbf{x})=\rho_0(\mathbf{x})+\delta\rho(\mathbf{x})$, the density increment $\delta\rho(\mathbf{x})$ transforming according to an (real) irreducible representation (IR) of G_0. In terms of the basis functions spanning the IR, one writes $\delta\rho(\mathbf{x})=\Sigma_i\gamma_i\phi_i(\mathbf{x})$. To identify the possible IR's of G_0, a choice is made of a vector $\mathbf{k}_0$ from a point of high symmetry of the Brillouin zone (assuming a transition to a commensurate phase). Given the observed structure of the superlattice [5], we pick the reciprocal vector

$$\mathbf{k}_0=\tfrac{2}{3}\mathbf{B}_1+\tfrac{1}{3}\mathbf{B}_2+\mathbf{C}\equiv\mathbf{A}_1+\mathbf{C}. \tag{3}$$

The vector $\mathbf{C}=(2\pi/c)\hat{\mathbf{e}}_\mathbf{z}$ provides the modulation along the columnar direction. The planar component $\mathbf{A}_1$ of $\mathbf{k}_0$ was shown to obey the Lifshitz condition in two dimensions [9] and it is clear from below that it also obeys Landau's condition. Application of all the 24 elements of D_{6h} on $\mathbf{k}_0$ determines that the associated little group is $G_{\mathbf{k}_0}=C_{3v}$. The character table of the (real) IR's τ of $G_{\mathbf{k}_0}$ shows the existence of two one-dimensional and one two-dimensional IR's. The star of $\mathbf{k}_0$ comprises three more vectors:

$$\mathbf{k}_0^*=\{\mathbf{k}_0,-\mathbf{k}_0,\mathbf{k}_1,-\mathbf{k}_1\} \tag{4}$$

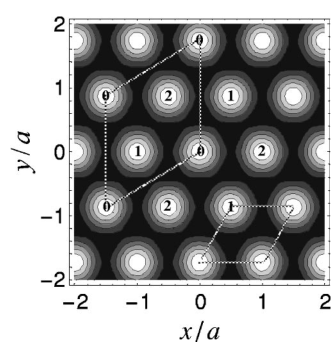

FIG. 1. Contour plot of the D_{hd} phase, after Eq. (2) (using $c_0=3/2$, $c_1=1$). Lighter regions are of higher density. Also shown are the D_{hd} and D_{ho} primitive cells and the column numbering.

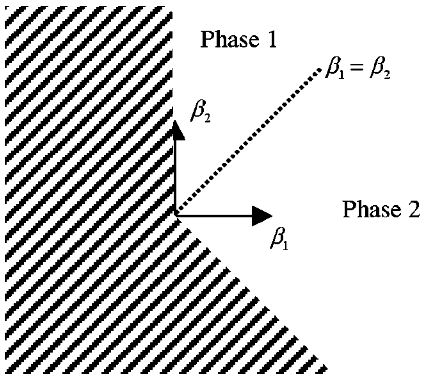

FIG. 2. Fourth-order phase diagram in the β_1-β_2 plane, showing the two possible phases 1 and 2. The hatched region has no stable phase.

with $\mathbf{k}_1 = \mathbf{A}_1 - \mathbf{C}$. $\mathbf{k}_0^*$ lies in a single plane. Note that the high-temperature symmetry group G_0 is identical to the one considered in [3], but since they investigated a transition to a phase with no order along the columnar direction, the continuous z translation remains unbroken.

Choosing an IR τ of C_{3v}, the basis functions are written as a product $\phi_i = u(\mathbf{k}_i)\Psi_\alpha(\mathbf{k}_i)$, where $\Psi_\alpha(\mathbf{k}_i)$ are scalar functions under translations and span a basis of τ, while $u(\mathbf{k}_i)$ is a linear combination, invariant under $G_{\mathbf{k}_0}$. At this point, we select the invariant representation $\tau = A_1$. In that case, $\Psi_\alpha(\mathbf{k}_i) = 1$ and the basis functions are

$$\phi_1 = \sum_{i=1}^{3} e^{i(\mathbf{Q}_i + \mathbf{C})\cdot \mathbf{x}}, \quad \phi_2 = \sum_{i=1}^{3} e^{i(\mathbf{Q}_i + \mathbf{C})\cdot \mathbf{x}}, \tag{5}$$

along with their complex conjugates. $\mathbf{Q}_i \in \{\mathbf{A}_1, \mathbf{A}_2, -(\mathbf{A}_1 + \mathbf{A}_2)\}$ span the new superlattice with $\mathbf{A}_2 = (\mathbf{B}_2 - \mathbf{B}_1)/3$. The density increment reads

$$\delta\rho(\mathbf{x}) = \sum_{i=1}^{2} [\gamma_i \phi_i(\mathbf{x}) + \text{c.c.}]. \tag{6}$$

$\delta\rho$ at a given site of the triangular lattice of columns has two components: an amplitude and a phase representing the vertical position of the maximum of $\delta\rho$. It is thus expected that the phase transition behavior is that of the planar (XY) model on a triangular lattice. On the other hand, we argue that it is the frustrated antiferromagnetic planar model since maxima of the density modulation on the three columns of a triangular plaquette may not be admitted at the same z value. A period c along the z axis is imposed. Hence, for the three-dimensional systems considered here, the analogy would be with a ferromagnetic stacking of the antiferromagnetic planar model on triangular layers.

Expanding the free energy F to fourth order, the following three invariants are generated:

$$F = \alpha(|\gamma_1|^2 + |\gamma_2|^2) + \frac{\beta_1}{4}(|\gamma_1|^4 + |\gamma_2|^4) + \frac{\beta_2}{2}(|\gamma_1|^2|\gamma_2|^2). \tag{7}$$

α, β_1, and β_2 are phenomenological coefficients. The form of the effectively two-dimensional free energy (7) has been known to arise from the C_{4v} image group [10]. From minimizing Eq. (7) for $\alpha < 0$ (i.e., $T < T_c$), two possible phases arise as shown in Fig. 2.

Phase 1 has $|\gamma_1| = 0$ and $|\gamma_2| = \sqrt{-\alpha/\beta_1}$ or $|\gamma_2| = 0$ and $|\gamma_1| = \sqrt{-\alpha/\beta_1}$. For both cases, with $\gamma_i = |\gamma_i| e^{i\varphi_i}$ ($i = 1,2$), the various values of φ_i correspond to equivalent density increments, shifted in the coordinate system along the z axis. After picking $\varphi_i = 0$, one has near T_c,

$$\delta\rho(\mathbf{x}) = 2\sqrt{-\alpha/\beta_1} \sum_{i=1}^{3} \cos[(\mathbf{Q}_i \pm \mathbf{C})\cdot \mathbf{x}]. \tag{8}$$

The two degenerate phases [$\pm$ from the signs in Eq. (8)] are related by an inversion in a plane perpendicular to the z axis and by rotations of $\pm\pi/3$ and π around the z axis. Their structure is of period c along the z axis. They are also invariant under translation by a superlattice vector of the form $n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ with n_1, n_2 integers and $\mathbf{a}_1 = \mathbf{b}_1 + \mathbf{b}_2$ and $\mathbf{a}_2 = 2\mathbf{b}_2 - \mathbf{b}_1$ the primitive vectors forming the basis for the superlattice (Fig. 1). Overall, it is verified that the phases 1 given by Eq. (8) are invariant over the symmetry operations of the space group 166: (D_{3d}^5). Physically, the modulations of columns 0, 1, and 2 (as shown in Fig. 1) in phase 1 (+) are shifted along z by 0, $c/3$, and $2c/3$, respectively (see Fig. 3).

Phases 1 are breaking a discrete chiral symmetry in addition to the continuous translation symmetry in the columnar direction. Indeed, let us label every corner of the triangles in the basal plane by the smallest displacement (positive or

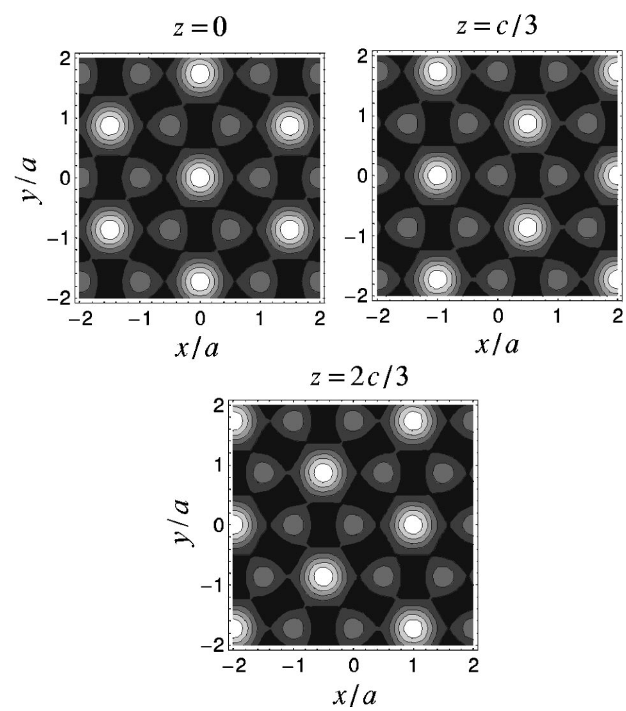

FIG. 3. Density profile $\rho(\mathbf{x})$ for phase 1, shown for $z = 0$, $c/3$, $2c/3$.

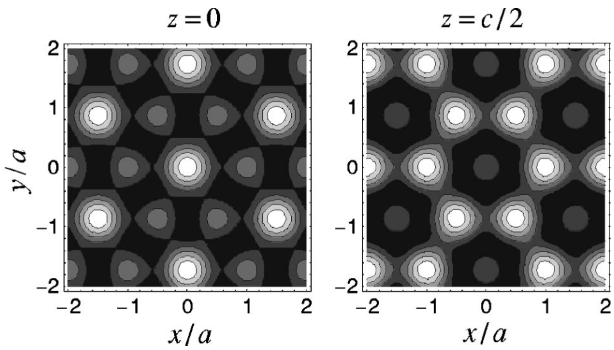

FIG. 4. Contour plot for density $\rho(\mathbf{x})$ in phase 2A, depicted at $z=0$ and $c/2$.

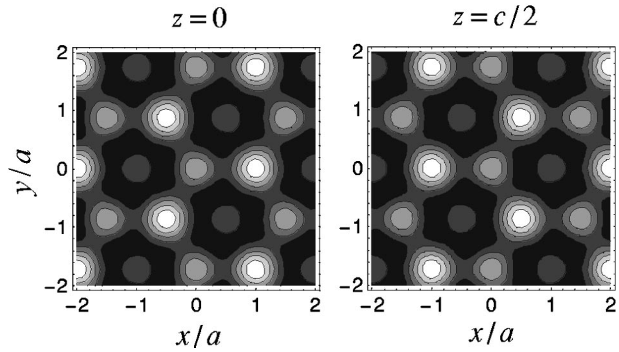

FIG. 5. Contour plot for density $\rho(\mathbf{x})$ in phase 2B, shown at $z=0$ and $c/2$.

negative) of their column in the columnar direction. Two sequences are then possible when the triangle is traversed in a clockwise direction: $(0,+c/3,-c/3)$ and $(0,-c/3,+c/3)$. The two phases, characterized by $\pm\mathbf{C}$ in Eq. (8), belong to two topologically distinct classes of patterns of the above sequences. Global translation in the columnar direction preserves these distinct classes. Under the above conditions, our system belongs to the same chiral universality class as the three-dimensional ferromagnetic stacking of antiferromagnetic planar spins on triangular layers.

In phase 2, $|\gamma_1|=|\gamma_2|$ and in terms of $\varphi_d=\varphi_2-\varphi_1$ and $\varphi_m=\frac{1}{2}(\varphi_1+\varphi_2)$ the density increment becomes

$$\delta\rho(\mathbf{x})=4\sqrt{-\alpha/(\beta_1+\beta_2)}\cos(\mathbf{C}\cdot\mathbf{x}-\tfrac{1}{2}\varphi_d)\times\sum_{i=1}^{3}\cos(\mathbf{Q}_i\cdot\mathbf{x}-\varphi_m). \tag{9}$$

Clearly, φ_d represents the freedom of arbitrarily moving the density along the z axis. Arbitrary values of φ_m, however, do not in general yield equivalent densities. In-plane translations by vectors $n_1\mathbf{b}_1+n_2\mathbf{b}_2$ (n_1,n_2 integers) are used to relate densities with φ_m's differing by $\pm 2\pi/3$, and rotations around the z axis by $\pm\pi/3$ connect densities with $\varphi_m\leftrightarrow\varphi_m+\pi$. Thus, the space of degenerate $\delta\rho(\mathbf{x})$ can be specified in the range $\varphi_m\in[0,\pi/6]$. To determine the stable configurations, the Landau free energy is expanded to sixth order with the addition of the following terms:

$$F_6=\frac{\beta_3}{6}(|\gamma_1|^6+|\gamma_2|^6)+\frac{\beta_4}{6}(\gamma_1^3\gamma_2^3+\gamma_1^{*3}\gamma_2^{*3})+\frac{\beta_5}{6}[|\gamma_1|^2|\gamma_2|^2(|\gamma_1|^2+|\gamma_2|^2)]. \tag{10}$$

In Eq. (10), only the second term depends on the phase angles and it is rewritten as $(\beta_4/6)|\gamma_1|^3|\gamma_2|^3\cos 6\varphi_m$. We note that this term is absent in the C_{4v} model. The condition $\partial F/\partial\varphi_m=0$ imposes that $\varphi_m=n\pi/6$ where n is an integer. Two situations are then possible, depending on the sign of β_4.

For $\beta_4<0$, $\varphi_m=2n\pi/6$ gives the stable phase 2A, invariant under the space group 191: (D_{6h}^1). In Fig. 4, the contour plots of the total density $\rho(\mathbf{x})$ (for $n=0$) show a shift of $c/2$ in occupancy between columns 0 and columns 1 and 2. The amount of density modulation is larger in columns 0 than for columns 1 and 2. Phase 2A breaks the continuous translation symmetry in the columnar direction but no discrete chiral symmetry is present in that case. All configurations belong to a single class of patterns convertible into each other by a global translation in the columnar direction combined with a lattice translation in the basal plane. The totally frustrated tripartite triangular lattice is transformed into a bipartite unfrustrated honeycomb lattice with the centers of the honeycombs forming a triangular lattice in a displaced plane. This phase is not predicted for the antiferromagnetic planar model on a triangular lattice. It is rendered possible in our model since there exists here the possibility of having modulations of different amplitudes on neighboring columns. The phase transition and critical properties are those of an antiferromagnetic planar model on a bipartite lattice. Phase 2A is the ordered columnar structure observed experimentally for HHTT [5], at least for the positional degrees of freedom. The transformation of the high-temperature fully frustrated tripartite triangular lattice into a low-temperature bipartite unfrustrated honeycomb lattice is sufficient to drive the system to a stable intercalated ordered columnar structure.

For $\beta_4>0$, phase 2B is obtained with $\varphi_m=(2n+1)\pi/6$. The resulting density is shown in Fig. 5 (for $n=1$). The corresponding space group symmetry of this phase is 194: (D_{6h}^4). It can be seen that in phase 2B columns 1 and 2 alternate in occupancy with their maxima separated by $c/2$, with no ordering in column 0. All degenerate ground states of phase 2B belong to one class of columnar patterns, all breaking the continuous translation symmetry along the z axis. No additional discrete chiral symmetry is present. This phase corresponds to a partially ordered phase of the planar model. Again, frustration drives the system to ordered phase with one-third of the columns remaining disordered.

An interesting topology emerges for the phase diagram in the T-β_1-β_4 space, for a given β_2. For $\beta_1<\beta_2$, two sheets of critical points extend, respectively, in the two regions $\beta_4<0$ and $\beta_4>0$. The line of critical points at $\beta_4=0$ and $\beta_1<\beta_2$ borders a sheet of first-order transitions connecting phases 2A and 2B below T_c. These two sheets of critical points belong to the nonchiral antiferromagnetic planar model ($n=2$) universality class in three dimensions.

For $\beta_1 > \beta_2$, a single sheet of critical points exists, all belonging to the chiral antiferromagnetic planar model ($n=2$) universality class in three dimensions. At $T=T_c$, $\beta_1=\beta_2$, and $\beta_4=0$, a multicritical point emerges where the two sets of sheets pinch the line of second-order transitions bordering the sheet of first-order transitions below T_c and $\beta_1=\beta_2$.

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