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Quasi-long-range order in columnar liquid crystals

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A mechanism is proposed for the effective free sliding of columns in an ordered columnar liquid crystal. Both positional and rotational degrees of freedom are involved and the free sliding, if it exists, would result from the shear deformation being accompanied by a rotational deformation of the opposite sign. Diagonalization of the rotational-positional total elastic energy leads to an effective curvature elastic term involving displacements in the columnar direction. Under such conditions, a quasi-long-range order of the positions of the molecules in the columnar direction would result. [S1063-651X(96)51711-3]

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The existence of columnar liquid crystal phases between the liquid and crystal phases for certain compounds composed of disk-shaped molecules is now very well established [1]. It is basically characterized by lattice ordering, in two dimensions, of liquidlike columns extending in the third dimension. There do exist cases [2], however, where high resolution x-ray results clearly established the existence of a phase with at least a partial ordering of both the positional and orientational degrees of freedom of the molecules inside the columns. This phase is often referred to as an H phase or a D_{ho} phase. Up to now, detailed high resolution x-ray studies of the ordered columnar phase have been only very few [3]. The conjecture is that the positional and orientational orderings are general behaviors for the D_{ho} phase to exist. However, the classification of this phase as a crystal phase or as a liquid crystal phase remains open [1,4–6]. Indeed with a root-mean-square displacement of the molecules in the columnar direction exceeding 30% of the intermolecular separation in this direction, the Lindemann melting formula [7] would generally be satisfied.

The continuum elasticity formalism, used up to now to understand the static deformation instabilities [8,9] and the Rayleigh scattering [10] in these systems, is based solely on the positional degrees of freedom, giving rise to the usual elastic energy terms from first-order derivatives and curvature terms from higher-order derivatives. The central question is the value of the shear elastic constant C_5 for columns sliding on each other in the direction of the columns in a hexagonal structure, a nonzero positive value of this last quantity leading to the stability of the three-dimensional crystal phase. As indicated above [2], in the D_{ho} phase, the internal rotational degrees of freedom of the molecules, in the plane perpendicular to the columnar direction, are expected to play an important and essential role. In typical systems showing the D_{ho} phase, nematic ordering is assumed to achieve its maximum value. In this Rapid Communication, it is shown that invoking a contribution to the total elastic energy from the rotational degrees of freedom allows for a mechanism for the vanishing of an effective shear elastic constant C_5^e with, however, the subsequent appearance of quasi-long-range order in the positions of the molecules along the columns. In this framework, the mean-square fluctuation of the displacements of the molecules in the direction of the columns is calculated and is shown to have a large relative value in good agreement with existing experimental data [2]. Contributions to the x-ray diffraction intensity coming from the thermal diffuse scattering under these conditions is predicted to turn the Bragg peaks into Bragg maxima with typical long tail decreases in reciprocal space. Finally, long-range orientational order is shown to be persistent.

Guided by the experimentally observed ordered structure proposed by Fontes *et al.* [2] for the H phase of the hexahexylthiotriphenylene compound (HHTT), we have studied [11] the fundamentals of the reconstructed three-column superlattice. This calculation allows for both helical ordering of a finite pitch P of the rotational degrees of freedom and a helicity pattern of three columns. We retain from this calculation and the experimental results of Fontes *et al.* [2] that the three-column superlattice sets in a helicity pattern also of period-3.

For the above helically ordered equilibrium conformation, based on the total rotationnal invariance in the basal triangular plane, the orientational elastic energy density $\mathcal{E}_o(\mathbf{r})$, including the coupling to the positional degrees of freedom, is written as

$$\begin{aligned}\mathcal{E}_o(\mathbf{r})=&\frac{1}{2}A_1[\varphi_x^2+\varphi_y^2]+\frac{1}{2}A_2\varphi_z^2+K_1[\varphi_{xx}+\varphi_{yy}]^2\\&+K_2[(\varphi_{xx}-\varphi_{yy})^2+4\varphi_{xy}^2]\\&+B_1[(\epsilon_{xx}+\epsilon_{yy})\varphi_z]+B_2[\epsilon_{xz}\varphi_x+\epsilon_{yz}\varphi_y],\end{aligned}\tag{1}$$

where $\varphi=\varphi(\mathbf{r})$ is the angular variable specifying the rotation, in the plane perpendicular to the columns, with respect to the equilibrium conformation. The z axis is taken along the columnar direction and the xy plane spans the triangular lattice. φ_α is a short notation for $\partial\varphi/\partial x_\alpha$ with $\alpha=x$, y, or z. $\varphi_{\alpha\beta}$ is a similar definition for the second-order derivatives. $\epsilon_{\alpha\beta}$ is the strain tensor components for the positional degrees

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of freedom. Notice the presence of terms linear in the gradients of φ which is a consequence of helically ordered equilibrium configuration. The first two terms of Eq. (1) are the two lowest-order terms resulting from the gradient of $\varphi(\mathbf{r})$ subjected to uniaxial symmetry of the system. The terms with the K_i coefficients are curvature terms for the orientational degrees of freedom. Starting from the microscopic Hamiltonian [11], the different parameters appearing in Eq. (1) have been calculated [12] and are shown to be the dominant terms coupling the positional and orientational degrees of freedom. The energy density $\mathcal{E}_o(\mathbf{r})$ describes slowly varying angular fluctuations of an helically ordered equilibrium configuration which retain in the long wavelength limit, the relative orientations of the three columns for the particular helicity pattern. As such they may be classified as ''soft deformations'' [13]. Fluctuations not conserving the relative orientations of the three columns and excitations having a soliton nature are not included since these ''hard deformations'' are expected to have an energy gap in the long wavelength limit and not contribute to destabilize the ground state configuration. To Eq. (1) is added the positional elastic energy density $\mathcal{E}_e(\mathbf{r})$ for a crystal of uniaxial symmetry [14]

$$\mathcal{E}_e(\mathbf{r})=\frac{1}{2}C_1\epsilon_{zz}^2+\frac{1}{2}C_2[\epsilon_{xx}+\epsilon_{yy}]^2+\frac{1}{2}C_3[(\epsilon_{xx}-\epsilon_{yy})^2+4\epsilon_{xy}^2]+\frac{1}{2}C_4[\epsilon_{zz}(\epsilon_{xx}+\epsilon_{yy})]+\frac{1}{2}C_5[\epsilon_{xz}^2+\epsilon_{yz}^2], \tag{2}$$

where C_i are the elastic constants, stressing that C_5 is the shear elastic constant for the columns being displaced parallel to each other in the columnar direction. A term linked to the bending of the columns has been omitted in Eq. (2) and may be shown to play no role in the mechanism proposed below. Indeed, the tilt of the molecules along bended columns is uncoupled to the displacements in the columnar direction to second order.

In Fourier space, the total elastic energy becomes

$$E=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\mathbf{q}\Bigg\{\left[C_1q_z^2+\frac{1}{4}C_5q_\perp^2\right]|u_z(\mathbf{q})|^2+\left[(C_2+C_3)q_\perp^2+\frac{1}{4}C_5q_z^2\right]|u_\perp(\mathbf{q})|^2+\left[C_3q_\perp^2+\frac{1}{4}C_5q_z^2\right]|u_\theta(\mathbf{q})|^2+[(C_4+C_5)q_zq_\perp]\mathrm{Re}[u_z(\mathbf{q})u_{q_\perp}^*(\mathbf{q})]+f(\mathbf{q})|\varphi(\mathbf{q})|^2+a(\mathbf{q})\mathrm{Re}[u_{q_\perp}(\mathbf{q})\varphi^*(\mathbf{q})]+b(\mathbf{q})\mathrm{Re}[u_z(\mathbf{q})\varphi^*(\mathbf{q})]\Bigg\},$$

where

$$a(\mathbf{q})=\left(B_1+\frac{1}{2}B_2\right)q_zq_\perp\,, \tag{3a}$$

$$b(\mathbf{q})=\frac{1}{2}B_2q_\perp^2\,, \tag{3b}$$

$$f(\mathbf{q})=A_1q_\perp^2+A_2q_z^2+(K_1+K_2)q_\perp^4\,, \tag{3c}$$

$(u_{q_\perp},u_\theta,u_z)$ are the $\mathbf{q}$ components of displacement in cylindrical coordinates. $\mathbf{q}_\perp$ is the vector component of $\mathbf{q}$ perpendicular to the columns. Re(β) stands for the real part of β. Two successive changes of variables [4] are necessary to diagonalize Eq. (3). First, the orientational variables are transformed according to

$$\varphi(\mathbf{q})=\Psi(\mathbf{q})-\frac{b}{2f}u_z(\mathbf{q})-\frac{a}{2f}u_{q_\perp}(\mathbf{q}). \tag{4}$$

Second, the diagonalization between $u_z(\mathbf{q})$ and $u_{q_\perp}(\mathbf{q})$ is completed by the transformation

$$u_{q_\perp}(\mathbf{q})=u_{q_\perp}'(\mathbf{q})-\frac{\gamma}{2g_2}u_z(\mathbf{q}), \tag{5}$$

where

$$\gamma(\mathbf{q})=\left(C_4+\frac{1}{2}C_5\right)q_zq_\perp-\frac{ab}{2f}, \tag{6a}$$

$$g_2(\mathbf{q})=(C_2+C_3)q_\perp^2+\frac{1}{4}C_5q_z^2-\frac{a^2}{4f}. \tag{6b}$$

The total elastic energy, in its diagonal form, becomes

$$E=\frac{1}{2}\frac{1}{(2\pi)^3}\int d\mathbf{q}\Bigg\{\left[g_1-\frac{\gamma^2}{4g_2}\right]|u_z(\mathbf{q})|^2+g_2|u_\perp'(\mathbf{q})|^2+\left[\frac{1}{4}C_5q_z^2+C_3q_\perp^2\right]|u_\theta(\mathbf{q})|^2+f|\Psi(\mathbf{q})|^2\Bigg\}, \tag{7}$$

where

$$g_1(\mathbf{q})=C_1q_z^2+\frac{1}{4}C_5q_\perp^2-\frac{b^2}{4f}. \tag{8}$$

The lowest-order terms, up to fourth order, for the coefficient of $|u_z(\mathbf{q})|^2$ are

$$g_1-\frac{\gamma^2}{4g_2}=\left\{C_1-\frac{[C_4+\frac{1}{2}C_5][C_4+\frac{1}{2}C_5-B_2(B_1+\frac{1}{2}B_2)/A_1]}{2(C_2+C_3)}\right\}\times q_z^2+\frac{1}{4}\left(C_5-\frac{B_2^2}{4A_1}\right)q_\perp^2+\frac{B_2^2(K_1+K_2)}{8A_1^2}q_\perp^4\,. \tag{9}$$

At this point, we bring into the model the central hypothesis which will characterize the H phase of a columnar liquid crystal from an elastic point of view: *in this phase, the columns slide on each other freely, having an effective shear elastic constant* C_5^e ($C_5^e=C_5-B_2^2/4A_1$) *equal to zero*. This is achieved by overall minimization of the total energy in the hexagonal ordered phase consequently determining the angular and positional characteristic lengths (pitch P and lattice spacings). In cases where such a minimization is not possible, the system would go directly from the disordered hexagonal phase to the crystal phase, a situation which cannot be rejected in the absence of a symmetry argument that would lead to an *a priori* vanishing of the shear elastic constant. As seen above, it is the coupling of the rotational degrees of freedom and vertical displacements which allows the above hypothesis to be realized. The justification for this hypothesis is *a posteriori* and was initially formulated on the basis of large values of the observed mean-square fluctuations of the positions of the molecules in the columns [2]. In any case there are good reasons to expect that C_5 is small in these systems, the main one being the lubrification role played by the n (usually $n=6$) partially flexible long chains attached to the hard cores and separating the columns. With this assumption, the coefficient of $|u_z(\mathbf{q})|^2$ becomes

$$g_1-\frac{\gamma^2}{4g_2}\simeq C_1q_z^2+Kq_\perp^4, \tag{10}$$

where $K=B_2^2(K_1+K_2)/8A_1^2$. Consequently, $\langle u_z^2(\mathbf{r})\rangle$ becomes

$$\langle u_z^2(\mathbf{r})\rangle=\frac{k_BT}{16\pi\sqrt{KC_1}}\ln(q_cL), \tag{11}$$

where k_B is Boltzmann's constant, q_c is a wave number of the order of the inverse of a molecular length in the columnar direction, and L is the size of the sample in the same direction. In agreement with de Gennes and Prost [4] we conclude with the absence of conventional long-range order in the columnar direction. However, we propose that quasi-long-range order exists where $\langle u_z^2(\mathbf{r})\rangle$ diverge logarithmically with the size L of the sample columnar direction. Using the microscopic Hamiltonian [11] and the angular and distance dependences of the intermolecular interaction parameters calculated by Cotrait *et al.* [15] for disklike molecules of the same family as the HHTT compound, the value of the parameter K is estimated to be of the order of 9×10^{-6} erg/cm. Using a typical value for C_1 ($C_1 = 10^8$ erg/cm^3) and $L=1$ mm, we get for $\sqrt{\langle u_z^2\rangle}$ a value of the order of 1 Å at 60 °C. It may be easily seen from Eqs. (7), (3c), and (6b) that the average values of the squares of $|u'_{q_\perp}(\mathbf{q})|$, $|u_\theta(\mathbf{q})|$, and $|\Psi(\mathbf{q})|$ stay finite as $L\rightarrow\infty$, in every case leading to a local fluctuation which is bounded and a small fraction of the range of definition of the variable. Such a general behaviour is observed experimentally in the high resolution x-ray results for the HHTT compound [16] in the H phase. Indeed the rms positional motions in both the columnar and basal directions are of the order of 1 to 2 Å, a large fraction of the intermolecular intracolumnar distance ($d=3.64$ Å) and a small fraction of the intercolumnar distance (typically 22 Å). As to the rms rotational fluctuations, a small value of the order of 5 to 10° is observed.

The most spectacular manifestation of the quasi-long-range order for the vertical displacement $u_z(\mathbf{r})$ shall appear in the shape of the Bragg maxima, as exemplified in a similar situation of algebraic decay of the correlation function in smectic A [17,18]. The x-ray scattering intensity is calculated for a three column triangular superlattice, all columns having an identical helicity and pitch P. The molecules are described by an angular octupolar moment. Contributions to the thermal diffuse scattering, in the neighborhood of a Bragg peak, from the fluctuating values of $|u'_{q_\perp}(\mathbf{q})|$, $|u_\theta(\mathbf{q})|$, and $|\Psi(\mathbf{q})|$ behave in the traditional manner, giving rise to a Debye-Waller factor for the intensity maxima and a q^{-2} decrease away from the Bragg peak positions. For Bragg peaks outside the basic plane and in particular the Bragg peak related to the periodicity of helical structure, the signature of the algebraic decrease of the correlation function manifests itself. Indeed for a momentum transfer given by

$$\mathbf{q}=\mathbf{G}_{hk}+3\left(\frac{2\pi}{P}\right)\hat{\mathbf{z}}+\mathbf{q}_\perp+q_z\hat{\mathbf{z}}, \tag{12}$$

where $\mathbf{G}_{hk}$ are the reciprocal lattice vectors for the reconstructed two-dimensional triangular lattice and $\mathbf{q}_\perp$ and q_z are now measured relative to the Bragg peak positions, we get that the intensity of diffused x ray has the following behavior:

$$I\sim\frac{1}{q_z^{2-\eta}}\quad\text{for }q_\perp=0, \tag{13a}$$

$$I\sim\frac{1}{q_\perp^{4-2\eta}}\quad\text{for }q_z=0. \tag{13b}$$

The parameter η is then given by

$$\eta=\frac{9\pi}{2P^2}\frac{k_BT}{\sqrt{KC_1}}. \tag{14}$$

Fluctuations of $u_z(\mathbf{r})$ being Gaussian, the parameters η for the successive Bragg maxima will increase as the square of the z component of the related Bragg peaks in reciprocal space. For the values of K and C_1 used above and $P\sim25$ Å [2], the dimensionless parameter η is of the order of 0.4, a value obtained with no adjustable parameters.

The above predictions for the x-ray scattering intensity are reached under the assumption that the effective shear elastic constant C_5^e vanishes in the H phase. As seen from the coupling term proportional to B_2 in Eq. (1), a relative vertical displacement of two columns is accompanied by a rotational displacement with the opposite sign. This fact is verified experimentally [16]. At this point, it is in order to recall that the three column reconstruction mentioned above [2] releases, at least partially, the geometrical frustration present for octupolar molecules on a triangular lattice. A simple model of gears and propellors on the resulting honeycomb lattice shows that the vertical displacement of one of the columns is favored energitically by a rotation of the opposite sign.

This sliding-rotating mechanism that allows the effective elastic constant C_5^e to vanish induces an effective curvature term which according to Eq. (10) could be written as

$$K\left(\frac{\partial^2u_z(\mathbf{r})}{\partial x^2}+\frac{\partial^2u_z(\mathbf{r})}{\partial y^2}\right)^2. \tag{15}$$

It originates from the rotational degrees of freedom and the coupling to the positional degrees of freedom. The existence of such a term, by analogy with smectic A, would be at the origin of the quasi-long-range behavior. Based on the experimental evidences mentioned above and the main conclusion of the present calculation, we propose that this fundamental behavior be looked at for using a high resolution x-ray analysis of the Bragg maxima in reciprocal space.

Notice that for columnar liquid crystals where the molecules would not be driven in equilibrium into a helical orientational structure, the curvature term (15) would be absent since its origin is the coupling terms in Eq. (1) permitted only because of the presence of helices. Subsequently, the ordered columnar phase would not be stabilized, at least by the above mechanism. It is also to be recalled that the curvature term linked to the bending of the columns is unable to stabilize quasi-long-range order in the direction of the columns.

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