

ARTICLES

Helix configurations in chiral hexatic liquid crystals

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In the hexatic- B^* phase the bonds defined by the long-range bond-orientational order are spiraling about the axis normal to the smectic layers. Apart from the bond ordering for the mass centers, a helical alignment of the molecular long axes characterized by a director field exists in some hexatic phases with tilted molecules. A continuum elastic distortion theory of liquid crystals predicts the existence of two possible configurations. If the commensurate configuration is stable, the director and the bond field are locked together, forming a common helix for both degrees of freedom. In the incommensurate state the director alignment differs from the alignment of the bonds so that two different helices occur. A phase diagram is proposed that includes three commensurate phases I^* , F^* , L^* and the incommensurate state. The incommensurate state becomes stable if the coupling between the director and the bond field is sufficiently small. [S1063-651X(97)06506-9]

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I. INTRODUCTION

The broken translational symmetry in a crystal necessarily entails long-range orientational order, since the crystalline axes define some preferred directions. A second type of orientational order results from the alignment of nonspherical molecules in liquid crystals. For example, the nematic state is characterized by the parallel alignment of long particles whose centers of gravity are randomly distributed as in an ordinary liquid. There is also another possibility to break the rotational symmetry of phases with molten crystalline lattice. The sixfold rotation axis of hexatic liquids is associated with the ordering of the lines joining neighboring atoms or molecules. Hexatic order has been observed in both two-dimensional and three-dimensional systems, for example, in free standing liquid crystal films, colloidal systems, in magnetic bubble arrays, and Langmuir-Blodgett films [1].

Especially, much work has centered around hexatic phases of liquid crystals [2–8]. The molecules of a hexatic- B phase are arranged in a stack of layers in which the molecular long axes are parallel to the layer normal. A crystalline lattice does not exist in the smectic layer planes, but a long-range bond-orientational order was found to occur. This order results from the alignment of the lines (bonds) connecting the centers of gravity of neighboring molecules. For illustrating this peculiar alignment of the bonds it is instructive to consider the local hexagon formed by a molecule and its six nearest neighbors (Fig. 1). In contrast to the disordered

smectic- A phase, which has no in-plane ordering, these hexagons are aligned macroscopically in the hexatic- B phase. Then the rotational symmetry is broken and the B phase has a sixfold symmetry axis parallel to the normal of the smectic layers. The orientation of the hexagonal clusters with respect to a fixed axis is determined by an angle η , as shown in Fig. 1. In order to describe both the strength of the bond-orientational order and the alignment of the hexagons the complex order parameter $\beta = |\psi| \exp(6i\eta)$ has been introduced [1]. The coefficient $|\psi|$ could be normalized in such a way that the condition $|\beta| = |\psi| = 1$ is satisfied for a perfectly ordered hexatic phase. In the smectic- A phase the hexagonal clusters are randomly oriented and β is equal to zero.

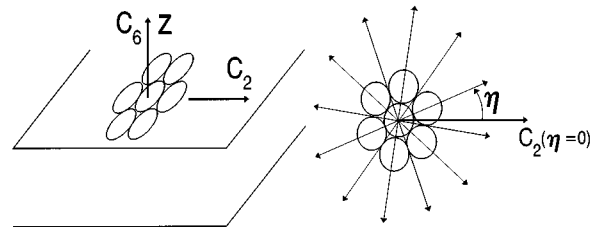


FIG. 1. In the hexatic- B phase the local hexagons formed by a molecule and its six nearest neighbors are aligned macroscopically. Besides the sixfold rotation axis perpendicular to the smectic layers there are also six twofold rotation axes parallel to the layer planes. A deviation of the local hexagon from its initial position due to elastic distortions can be defined by the angle η .

A. Elastic distortion energy associated with the rotation of the bond net

The equation $C_6\beta = \beta$ (where $C_6\beta$ is the resulting structure after a $2\pi/6$ rotation) symbolizes that a rotation of the whole hexatic structure about the z axis by an angle $2\pi/6$ does not change the order parameter. On the other hand, using Fig. 1, a simple geometrical consideration shows that turning around a C_2 axis inverts the z axis and transforms the angle η into $\eta \rightarrow m\pi/3 - \eta$ (m , integer). Hence it follows that $C_2\beta = \beta^*$ and $z \rightarrow -z$. Mirror planes existing in the nonchiral hexatic- B phase transform β into β^* without changing z . In this case only two quadratic terms $\beta\beta^* = |\psi|^2$ and $\partial_z\beta\partial_z\beta^* = |\partial_z\psi|^2 + 36|\psi|^2(\partial_z\eta)^2$ are found to be invariant. If the material consists of chiral molecules mirror planes are forbidden, then the Lifshitz term $L = i(\beta\partial_z\beta^* - \beta^*\partial_z\beta) = -6|\psi|^2\partial_z\eta$ has to be taken into account additionally. As the gradient $|\partial_z\psi|$ is negligibly small beyond the critical temperature of the Sm- A –Sm- B phase transition, we arrive at the elastic free energy density $f_B = \frac{1}{2}K_6(\partial_z\eta)^2 - R_6\partial_z\eta$, where the notation $K_6 = 72K_6^0|\psi|^2$ and $R_6 = 6R_6^0|\psi|^2$ is used (K_6^0 and R_6^0 are material constants). Minimizing the free energy $\int dz f_B$ yields $\eta(z) = qz + \text{const}$ with $q = R_6/K_6$. Obviously, the bond net of the chiral hexatic- B phase winds around the axis normal to the smectic layers. This result is already discussed in Ref. [8] using the Orsay group formulation of the continuum theory for smectic phases.

We mention that nonhomogeneous ground states were also found in other chiral systems with bond-orientational order. Periodic distortions visible by a striped texture are stable in Langmuir monolayers [9]. The helical alignment of the bonds in a chiral nematic phase with bond-orientational order was recently discussed [10]. This structure is similar to the helical alignment of the bonds predicted for the chiral hexatic- B phase.

B. Elastic free energy associated with the azimuthal tilt angle

There are also hexatic phases with molecules tilted towards the smectic layer planes [2–7]. It is useful to introduce a unit vector \mathbf{n} called the director (Fig. 2), which is parallel to the local direction of the long molecular axes. The smectic phases I , F , and L are distinguished by the director orientation with respect to the bonds. In the smectic- I phase (Sm- I) the director is tilted towards an apex of the local hexagon, while in the smectic- F phase (Sm- F) the tilt direction is locked halfway between two local bonds. The smectic- L phase is defined by an asymmetrical tilt direction. Only the phases Sm- I and Sm- F were identified in thermotropic liquid crystal compounds. However, the smectic- L phase was recently detected in the phase sequence of a phosphatidylcholine multimembrane [7].

The complex order parameter $\xi = \theta \exp(i\phi)$ is useful to characterize the tilt order in smectic liquid crystals [11]. We assume that the polar angle θ remains constant in a distorted sample, since the torque required for changing the azimuthal director rotation is much lower. Then the free energy density due to director rotations depends on the spatial derivatives of the azimuthal angle ϕ . For our purposes it is sufficient to consider distortions with gradients parallel to the z axis. In this case the bilinear expressions $\partial_z\xi\partial_z\xi^* = \theta^2(\partial_z\phi)^2$ and

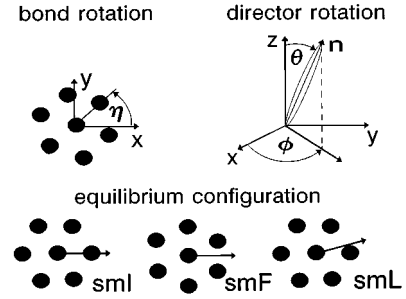


FIG. 2. The orientations of the director and the bonds are characterized by the angles ϕ and η , respectively. The nonchiral phases I , F , and L are distinguished by different equilibrium tilt directions of the long molecules with respect to the bonds. In the chiral phases I^* , F^* , and L^* the director and the bonds are winding uniformly around the z axis so that the configuration in each smectic layer is the same as in the corresponding nonchiral phases. If the incommensurate configuration is stable, the director and the bond orientations are out of phase.

$L' = i(\xi\partial_z\xi^* - \xi^*\partial_z\xi) = -\theta^2\partial_z\phi$ lead to the free energy density $f_C = \frac{1}{2}K_1(\partial_z\phi)^2 - R_1\partial_z\phi$ while $K_1 = K_1^0\theta^2$ and $R_1 = R_1^0\theta^2$ (K_1^0 and R_1^0 are material constants). Minimizing the free energy $\int dz f_C$, the helical director alignment $\phi(z) = \hat{q}z + \text{const}$ with $\hat{q} = R_1/K_1$ is found to be stable. This configuration exists in the smectic- C^* phase, as there the bond-orientational order is rather weak [12]. When the hexatic ordering becomes remarkably strong, however, the helical alignment can be modified due to the coupling between the director and the bond field.

C. Free energy for elastic distortions including coupling terms

Finally, the free energy density is written as $f = f_B + f_C + f_{BC}$, where the additional term f_{BC} characterizes the coupling between the director and the bond field. Modifying slightly the free energy proposed by Selinger and Nelson [3], we get

$$F = \frac{1}{L} \int_0^L dz \left[\frac{1}{2} K_1 (\partial_z \phi)^2 + \frac{1}{2} K_6 (\partial_z \eta)^2 + K_{16} \partial_z \phi \partial_z \eta - R_1 \partial_z \phi - R_6 \partial_z \eta + V(\phi - \eta) \right], \quad (1)$$

where the term proportional to K_{16} and the contribution

$$V(\phi - \eta) = -h_6 \cos 6(\phi - \eta) - h_{12} \cos 12(\phi - \eta) \quad (2)$$

account for the elastic and the direct coupling between the director and the bond field, respectively. Obviously, expression (2) does not exactly display the symmetry of the structure, as the local hexagon is elongated parallel to the tilt direction of the molecules. Thus a sixfold symmetry axis C_6 for the bond net cannot exist. But for small tilt angles θ the simplified expression (2) should be sufficient for describing the essential physics of the system [3].

In the nonchiral phases Sm- I , Sm- F , and Sm- L the linear gradient terms $-R_1\partial_z\phi$ and $-R_6\partial_z\eta$ are equal to zero and both the director and the bonds are homogeneously aligned. The configuration in the corresponding chiral phases I^* ,

F^* , and L^* (an asterisk indicates chirality) is different due to the linear gradient terms, which produce a helical alignment of the director and the bonds.

II. HELICAL ALIGNMENT FOR STRONG AND WEAK COUPLING CONSTANTS

Concerning the helical alignment in the smectic phases I^* , F^* , and L^* , two configurations are possible. The director can be locked in the hexagonal net so that only one helix describing a uniform spiraling of the director and the bonds is present. This commensurate configuration is expected to be stable if the coupling between the director and the bonds is relatively strong. Otherwise, if this coupling is sufficiently weak, both degrees of freedom are out of phase. Then the resulting incommensurate structure is more complex, characterized by a different helical alignment of the director and the bonds. Let us consider two borderline cases to illuminate the alignment in the incommensurate and the commensurate states. If the coupling is rather strong the difference $\phi - \eta$ in chiral hexatics is the same as in the nonchiral phases Sm- I , Sm- F , and Sm- L . Minimizing the potential (2) we get $\eta(z) = \phi(z) + \eta_0$, where the constant angle η_0 is defined by

$$\begin{aligned} \eta_0 &= 0 \quad \text{for } h_6 > 0 \quad \text{and } 4h_{12} > -h_6 \quad (\text{phase } I^*), \\ \eta_0 &= \pi/6 \quad \text{for } h_6 < 0 \quad \text{and } 4h_{12} > h_6 \quad (\text{phase } F^*), \\ \cos 6\eta_0 &= -h_6/(4h_{12}) \quad \text{for } h_{12} < 0 \\ \text{and } |h_6/(4h_{12})| &< 1 \quad (\text{phase } L^*). \end{aligned} \quad (3)$$

Considering additionally the terms with spatial derivatives in the free energy (1), the helical alignment

$$\phi(z) = qz \quad \text{and} \quad \eta(z) = qz + \eta_0, \quad (4)$$

with

$$q = \frac{R_1 + R_6}{K_1 + K_6 + 2K_{16}}$$

is found to be stable.

In the incommensurate state the director helix and the bond helix form a more complex structure [13]. As an illustration we consider the borderline case which corresponds to a very weak direct coupling between the director and the bonds ($|h_6| \rightarrow 0$ and $|h_{12}| \rightarrow 0$). Assuming that $|h_6| = |h_{12}| = 0$ and minimizing the free energy (1) yields the configuration

$$\phi(z) = q_1 z \quad \text{and} \quad \eta(z) = q_6 z + \hat{\eta}_0, \quad (5)$$

where $q_1 = (K_6 R_1 - K_{16} R_6)/(K_1 K_6 - K_{16}^2)$, $q_6 = (K_1 R_6 - K_{16} R_1)/(K_1 K_6 - K_{16}^2)$, and $\hat{\eta}_0$ is an arbitrary constant. Obviously, the relations (5) describe two independent helices with different pitch (period). However, it should be mentioned that a complete decoupling of the director and the bonds, as suggested by these relations, is not possible. If the coupling constants h_6 and h_{12} are not exactly equal to zero, some correlations between ϕ and η still remain.

III. THE COMMENSURATE-INCOMMENSURATE TRANSITION

A more complete description of the helical alignment in the incommensurate state requires the solution of the Eulerian equation associated with the functional (1). For this purpose it is useful to apply the linear transformation [2,3]

$$\Lambda = 6(\alpha\eta + \beta\phi) \quad \text{and} \quad \Omega = 6(\phi - \eta), \quad (6)$$

where $\alpha = (K_6 + K_{16})/K$, $\beta = 1 - \alpha$, and $K = K_1 + K_6 + 2K_{16}$. After evaluating Λ and Ω , the angles ϕ and η will be obtained from the inverse transformations $\phi = [\Lambda + \alpha\Omega]/6$ and $\eta = [\Lambda - \beta\Omega]/6$. Omitting a constant term, the free energy (1) is transformed into

$$F = \frac{\Delta}{36KL} \int_0^L dz \left[\frac{1}{2} (\Omega_z - Q_1)^2 + \frac{K^2}{2\Delta} (\Lambda_z - Q_6)^2 + W(\Omega) \right], \quad (7)$$

where the notation

$$\begin{aligned} W(\Omega) &= -H_6 \cos \Omega - H_{12} \cos 2\Omega, \\ \Delta &= K_6 K_1 - K_{16}^2 > 0, \quad H_6 = \frac{36K h_6}{\Delta}, \\ H_{12} &= \frac{36K h_{12}}{\Delta}, \quad Q_6 = \frac{6(R_1 + R_6)}{K} \end{aligned}$$

and

$$Q_1 = \frac{6K(\alpha R_1 - \beta R_6)}{\Delta}$$

is used. Minimizing the functional (5) with respect to Λ , we obtain straightforwardly

$$\Lambda = Q_6 z + \Lambda_6, \quad (8)$$

where Λ_6 is an integration constant. It remains to minimize the functional

$$\hat{F} = \frac{\Delta}{36KP} \int_0^P dz \left[\frac{1}{2} (\Omega_z - Q_1)^2 + W(\Omega) \right], \quad (9)$$

where we have replaced the integration interval L by the distance P within which Ω changes by 2π . If $P \ll L$ the boundary conditions for $z=0$ and L do not remarkably influence the configuration in the bulk. An expression for the free energy, possessing the same mathematical structure as Eq. (9), was studied by Dimitrienko and Belyakov [14] for describing the helical director alignment in the smectic- C^* phase in an electric field. Thus we can mainly adapt these calculations to our problem. The Eulerian equation

$$\Omega_{zz} - H_6 \sin \Omega - 2H_{12} \sin 2\Omega = 0 \quad (10)$$

is a necessary condition for a minimum of the free energy contribution (9). Equation (10) has the simple solution $\Omega = 6\eta_0$, where the angle η_0 is defined by the relations (3). This solution corresponds to the commensurate helical direc-

tor and bond alignment (4). Now let us look for nontrivial solutions of the differential equation (10). The first integral is found to be

$$\frac{1}{2}\Omega_z^2 = W(\Omega) + \omega, \quad (11)$$

and a second integration leads to

$$\int_0^\Omega \frac{d\Omega'}{\pm \sqrt{2\omega + 2W(\Omega')}} = z - z_0, \quad (12)$$

where the integration constant ω will be obtained from the condition that the functional (9) is a minimum. Close to the threshold of the commensurate-incommensurate transition Eq. (12) describes a soliton lattice, e.g., a sequence of domains within which Ω is almost constant over long distances. For $H_6 > 0$ these domains are separated by a regular array of walls. At each wall the difference $\phi - \eta = \Omega/6$ switches by $\pi/3$ [13]. For $H_{12} < 0$ and $|H_6/(4H_{12})| < 1$ this picture is slightly modified [14], as the soliton lattice near to the threshold is composed of two wall types; after a switch $-\eta_0 \rightarrow +\eta_0$ of the angle $\Omega/6 = \phi - \eta \pmod{\pi/3}$ follows a second switch $\eta_0 \rightarrow 2\pi - \eta_0$. A further peculiarity refers to the commensurate region in the phase diagram. It was shown that a single domain wall can survive in the commensurate state [14]. However, a wall, where the difference $\phi - \eta$ changes by a small value ($< 30^\circ$), would be hardly detectable in a macroscopic sample with a helical alignment of the director and the bonds. Therefore we do not consider this wall, which could appear in the L^* phase.

The distance

$$P = \int_0^{2\pi} \frac{d\Omega'}{\pm \sqrt{2\omega + 2W(\Omega')}}, \quad (13)$$

within which the angle Ω changes by 2π is finite in the incommensurate state. When the transition to the commensurate state is approached, the denominator in the integral (13) tends to zero and the period P diverges. Using the first integral (11), the functional (9) is transformed into

$$\frac{36K}{\Delta} \hat{F} = \frac{1}{P} \int_0^{2\pi} \pm \sqrt{2\omega + 2W(\Omega)} d\Omega - \frac{2\pi Q_1}{P} + \frac{1}{2} Q_1^2.$$

Stability requires that \hat{F} as a function of ω is a minimum. A condition necessary for a minimum is

$$\begin{aligned} \frac{36K}{\Delta} \frac{\partial \hat{F}}{\partial \omega} &= \frac{1}{P} \left[\int_0^{2\pi} \frac{d\Omega}{\pm \sqrt{2\omega + 2W(\Omega)}} - P \right] \\ &- \frac{1}{P^2} \frac{\partial P}{\partial \omega} \left[\int_0^{2\pi} \pm \sqrt{2\omega + 2W(\Omega)} d\Omega - 2\pi Q_1 \right] = 0. \end{aligned}$$

Taking into account the relation (13), we obtain the equation

$$\int_0^{2\pi} \pm \sqrt{2\omega + 2W(\Omega)} d\Omega = 2\pi Q_1 \quad (14)$$

connecting the integration constant ω with Q_1 . Comparing both sides of Eq. (14), the correct sign before the root $\sqrt{2\omega + 2W(\Omega)}$ in Eqs. (12) and (13) is found to be depen-

dent on the sign of Q_1 . Generally, Eq. (14) has to be solved numerically, but the threshold condition for the commensurate-incommensurate transition can be expressed analytically in a similar way as the critical electrical field for unwinding the director helix of a smectic- C^* phase [14]. Since the potential $W(\Omega)$ is minimized for $\Omega = 6\eta_0$, Eq. (14) is solvable only in those cases where the condition $\omega + W(6\eta_0) > 0$ is satisfied. This condition guarantees that the square root $\sqrt{2\omega + 2W(\Omega)}$ is a real number for $0 \leq \Omega < 2\pi$. Then the incommensurate state characterized by Eq. (12) turns out to be stable. On the other hand, if $\omega + W(6\eta_0) < 0$ the commensurate configuration (4) is the only possible state. Therefore the condition $\omega = -W(6\eta_0)$ is satisfied at the threshold of the commensurate-incommensurate transition. Using this condition, the equation

$$\int_0^{2\pi} \sqrt{-2W(6\eta_0) + 2W(\Omega)} d\Omega = 2\pi |Q_1| \quad (15)$$

allows us to derive analytical threshold formulas (see the Appendix). Three different cases have to be considered.

If $H_{12} > 0$ Eq. (15) has the solution

$$H_{12} = \frac{\pi^2 Q_1^2 (\sinh p)^4}{4(\sinh 2p + 2p)^2} \quad \text{and} \quad H_6 = \pm 4H_{12}/(\sinh p)^2, \quad (16)$$

where p is a parameter ($0 < p < \infty$). For $H_{12} < 0$ and $|h_6/(4h_{12})| > 1$ the solution is expressed as

$$-H_{12} = \frac{\pi^2 Q_1^2 (\sin p)^4}{4(\sin 2p + 2p)^2} \quad \text{and} \quad H_6 = \pm 4(-H_{12})/(\sin p)^2, \quad (17)$$

and, finally, if $H_{12} < 0$ and $|h_6/(4h_{12})| < 1$, we obtain

$$-H_{12} = \left\{ \frac{Q_1}{[4(\tan \hat{p} - \hat{p})/\pi + 2]\cos \hat{p}} \right\}^2, \quad (18)$$

$$H_6 = \pm 4(-H_{12})\cos \hat{p},$$

where $0 < \hat{p} < \pi/2$.

IV. DISCUSSION OF THE PHASE DIAGRAM

The threshold formulas (16)–(18) of the commensurate-incommensurate transition are suitable to construct a phase diagram for chiral hexatic phases. Introducing the dimensionless coupling parameters $\hat{h}_6 = H_6/Q_1^2 = \Gamma h_6$ and $\hat{h}_{12} = H_{12}/Q_1^2 = \Gamma h_{12}$ where

$$\Gamma = \frac{(K_1 + K_6 + 2K_{16})(K_1 K_6 - K_{16}^2)}{[(K_6 + K_{16})R_1 - (K_1 + K_{16})R_6]^2}, \quad (19)$$

we obtain the lower diagram depicted in Fig. 3. In the droplet-shaped region the incommensurate state characterized by two different helices for the director and the bond field is stable. Outside this region the difference $\phi - \eta$ is constant and the relations (4), which describe the commensurate phases I^* , F^* , and L^* , are applicable.

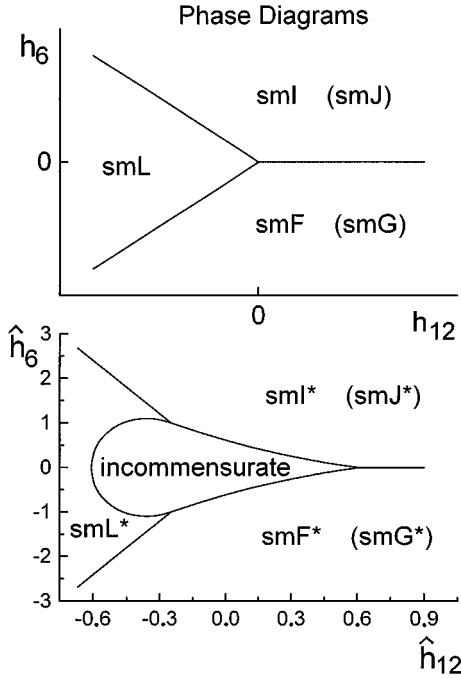


FIG. 3. Phase diagrams for nonchiral, chiral hexatic, and crystalline smectic phases with tilted molecules. The upper diagram, which refers to nonchiral materials, is proposed by Selinger and Nelson [3] in the framework of a mean field model for hexatic smectic phases. The lower diagram shows that chirality leads to an additional phase region, characterized by an incommensurate helical alignment of the director and the bonds.

In suitably designed chiral compounds or nonracemic mixtures the commensurate-incommensurate transition could be driven by altering the helical pitch which depends on the concentration and the temperature. Substances with a short pitch could be good candidates for the formation of the incommensurate state. According to Fig. 3 the incommensurate phase region is located in a restricted region around the origin, where the modified coupling parameters \hat{h}_6 and \hat{h}_{12} are sufficiently small. It is instructive to estimate the dependence of \hat{h}_6 and \hat{h}_{12} on the tilt angle θ . The coefficients h_6 and h_{12} entering into the potential (2) can be expressed in terms of the order parameters ξ and β . In the framework of a Landau-Ginzburg theory the free energy density appropriate for describing tilted smectic phases contains the coupling term [15]

$$\frac{1}{2} h_6^0 [\xi^6 \beta^* + (\xi^*)^6 \beta] = h_6^0 \theta^6 |\psi| \cos 6(\phi - \eta).$$

The additional coupling term

$$\frac{1}{2} h_{12}^0 [\xi^{12} (\beta^*)^2 + (\xi^*)^{12} \beta^2] = h_{12}^0 \theta^{12} |\psi|^2 \cos 12(\phi - \eta)$$

should be important if the material constant h_6^0 becomes a small quantity in the vicinity of the Sm-I–Sm-F phase transition temperature [3]. A comparison of these expressions with the coefficients in potential (2) suggests that the relations $h_6 = h_6^0 \theta^6 |\psi|$ and $h_{12} = h_{12}^0 \theta^{12} |\psi|^2$ are valid. Similarly, the product LL' of the Lifshitz terms L and L' yields $K_{16} = K_{16}^0 \theta^2 \psi^2$. Furthermore, taking into account the previously

found relations $K_1 = K_1^0 \theta^2$, $R_1 = R_1^0 \theta^2$, $K_6 = 72 K_6^0 |\psi|^2$, and $R_6 = 6 R_6^0 |\psi|^2$, we obtain the expansions

$$\begin{aligned} \hat{h}_6 &= C_1 |\psi| \theta^4 + C_2 |\psi|^{-1} \theta^6 + \dots, \\ \hat{h}_{12} &= C_3 |\psi|^2 \theta^{10} + C_4 \theta^{12} + \dots, \end{aligned} \quad (20)$$

where the coefficients C_n ($n=1, \dots, 4$) do not depend on θ and $|\psi|$. Obviously, by reducing the tilt angle θ the incommensurate phase region depicted in Fig. 3 could be achieved. It should also be noted that the coefficient h_6^0 is equal to zero at the Sm- J^* –Sm- F^* phase transition temperature. In a vicinity of this transition temperature the incommensurate state is predicted to be stable if $\hat{h}_{12} < \pi^2/16$.

In the smectic phases Sm- J^* and Sm- G^* the bond net is replaced by a crystalline lattice. The tilt direction of the long molecules with respect to the lattice is analogous to Sm- J^* and Sm- F^* . However, because of the crystalline order, the elastic constant K_6 is considered infinite [2,3]. Consequently, the angle η is constant and the free energy (1) may be written as

$$\begin{aligned} F = \frac{1}{L} \int_0^L dz \left[\frac{1}{2} K_1 (\partial_z \phi)^2 - R_1 \partial_z \phi - h_6 \cos 6(\phi - \eta_0) \right. \\ \left. - h_{12} \cos 12(\phi - \eta_0) \right]. \end{aligned}$$

Using the modified notation $\hat{h}_6 = (K_1/R_1^2) h_6$ and $\hat{h}_{12} = (K_1/R_1^2) h_{12}$ the phase diagram depicted in Fig. 3 remains valid. The commensurate state is now characterized by a homogeneous alignment of both the director and the bonds ($\phi=0$ and $\eta=\eta_0$). The condition $\eta=\text{const}$ is also satisfied for the incommensurate state, but the director winds around the z axis, forming a helix. It is relatively easy to distinguish between the helical and the homogeneous director alignment in smectic crystals. For instance, the helical alignment of the director causes a very large optical activity and a selective reflection of light. Kuscinsky and Stegemeyer [16] claimed that the director configuration is different in two crystalline smectic phases of the compound 4-(2'-methylbutyl) phenyl-4'- n -oktylbiphenyl-4-carboxylate (CE8). A helical director alignment was found in one of these phases, which was called Sm- J^* in Ref. [16]. According to the classification used in Fig. 3, this crystalline phase should be allocated to the incommensurate state. On the other hand, in the smectic- G^* phase of CE8 the director was found to be homogeneously aligned in accordance with the expected behavior of a commensurate crystalline configuration.

Unfortunately, the slight differences between the helical director configurations in the commensurate and the incommensurate states of liquid crystalline hexatic phases are hardly observable by simple optical experiments. It is reasonable to assume that the director and the bond field in thermotropic liquid crystals are usually locked together, forming the commensurate configuration. More sophisticated experiments are necessary to clarify whether the liquid crystalline hexatic phases are always commensurate. The commensurate-incommensurate transition would be accompanied with a texture change in thick homeotropically aligned smectic films sandwiched between parallel plates.

Texture observations of CE8 indicated a reorganization of the director helix [16], although the enthalpy of this phase transition was found to be undetectably small. A further characterization of this transition requires detailed optical experiments. Investigating the propagation of a light beam, which is sent parallel to the helical axis (z), would provide some information on the helical alignment of the director. The transmission and reflection of light in chiral smectic liquid crystals is strongly wavelength dependent and could be analyzed by applying the same methods as used for cholesteric liquid crystals [17]. In the incommensurate phase the azimuthal director angle ϕ , which is described implicitly by Eqs. (6), (8), and (12), is no longer a simple linear function of the coordinate z . Consequently, the optical properties of the ideal director helix in the commensurate state are expected to be different from the properties of the disturbed helix in the incommensurate state. It would be interesting to investigate how the director is connected to the bond net in different chiral materials.

V. CONCLUSION

In conclusion, we found that two different configurations exist in chiral hexatic smectic phases with tilted molecules. If the commensurate configuration is stable, the director and the bond orientation are locked together, forming a common helix. In the incommensurate state both degrees of freedom are decoupled so that two different helices occur. A transition from the commensurate to the incommensurate state can be driven by reducing the coupling between the director and the bond field. This coupling is weak in the vicinity of the smectic- I^* -smectic- F^* phase transition temperature and if the molecular tilt angle is sufficiently small. For crystalline smectic phases the incommensurate state is characterized by the existence of a director helix, while this helix is completely unwound in the commensurate state.

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APPENDIX: THRESHOLD CONDITIONS FOR THE INCOMMENSURATE STATE

Equation (15) is solved for three different cases.

(I) *Case* $H_{12} > 0$. If $H_{12} > 0$ we can choose $\eta_0 = 0$ for $H_6 > 0$ and $\eta_0 = \pi/6$ for $H_6 < 0$ and obtain

$$\begin{aligned} & \sqrt{-2W(6\eta_0) + 2W(\Omega)} \\ &= \sqrt{2H_6(1 - \cos\Omega) + 2H_{12}(1 - \cos 2\Omega)} \quad \text{for } H_6 > 0, \end{aligned}$$

$$\begin{aligned} & \sqrt{-2W(6\eta_0) + 2W(\Omega)} \\ &= \sqrt{-2H_6(1 + \cos\Omega) + 2H_{12}(1 - \cos 2\Omega)} \quad \text{for } H_6 < 0, \end{aligned}$$

or written differently

$$\begin{aligned} & \sqrt{-2W(6\eta_0) + 2W(\Omega)} \\ &= 2|\sin(\Omega/2)|\sqrt{H_6 + 4H_{12}\cos^2(\Omega/2)}, \\ & \sqrt{-2W(6\eta_0) + 2W(\Omega)} \\ &= 2|\cos(\Omega/2)|\sqrt{-H_6 + 4H_{12}\sin^2(\Omega/2)}. \end{aligned}$$

Using the substitutions $y = \pm \cos(\Omega/2)$ and $y = \pm \sin(\Omega/2)$ Eq. (15) is transformed into

$$\begin{aligned} 2\pi|Q_1| &= 8 \int_0^1 dy \sqrt{|H_6| + 4H_{12}y^2} = 16\sqrt{H_{12}} \int_0^1 dy \sqrt{a^2 + y^2} \\ &= 8\sqrt{H_{12}}[\sqrt{a^2 + 1} + a^2 \operatorname{arcsinh}(1/a)], \end{aligned}$$

where

$$a^2 = \frac{|H_6|}{4H_{12}}.$$

The substitution $p = \operatorname{arcsinh}(1/a)$ which implies $\sqrt{a^2 + 1} = \cosh p / \sinh p$ and $a^2 = 1/(\sinh p)^2$, leads to the result

$$2\pi|Q_1| = 4\sqrt{H_{12}} \frac{\sinh 2p + 2p}{(\sinh p)^2}, \quad (\text{A1})$$

$$|H_6| = 4H_{12}/(\sinh p)^2,$$

which is equivalent to the relations (16).

(II) *Case* $H_{12} < 0$ and $|H_6/4H_{12}| > 1$. Choosing η_0 as in case (I) Eq. (A1) is transformed into

$$2\pi|Q_1| = 16\sqrt{-H_{12}} \int_0^1 dy \sqrt{b^2 - y^2},$$

where the notation $b^2 = |H_6|/[4(-H_{12})]$ is used. Performing the integration and introducing a parameter $\bar{p} = \arcsin(1/b)$ leads to the result

$$2\pi|Q_1| = \frac{4\sqrt{-H_{12}}(\sin 2\bar{p} + 2\bar{p})}{(\sin \bar{p})^2}, \quad (\text{A2})$$

$$|H_6| = 4(-H_{12})/(\sin \bar{p})^2,$$

which is equivalent to the relations (17). The result (A2) can also be obtained by replacing p by $\bar{p}/\sqrt{-1}$ in Eq. (A1).

(III) *Case* $H_{12} < 0$ and $|H_6/4H_{12}| < 1$. Minimizing the potential $W(\Omega)$ yields

$$\cos \Omega_0 = -\frac{H_6}{4H_{12}},$$

where $\Omega_0 = 6\eta_0$. Now the positive square root can be written as

$$\sqrt{-2W(\Omega_0) + 2W(\Omega)} = 2\sqrt{-H_{12}}|\cos \Omega - \cos \Omega_0|.$$

Without loss of generality we can assume that $-\pi < \Omega_0 \leq \pi$. For $0 < \Omega_0 \leq \pi$ Eq. (15) is expressed as

$$2\pi|Q_1| = 2\sqrt{-H_{12}} \left\{ \int_{\Omega_0}^{2\pi-\Omega_0} (\cos\Omega_0 - \cos\Omega) d\Omega + \int_{2\pi-\Omega_0}^{2\pi+\Omega_0} (\cos\Omega - \cos\Omega_0) d\Omega \right\}.$$

Thus we get $2\pi|Q_1| = 2\sqrt{-H_{12}}(4\sin\Omega_0 + 2\pi\cos\Omega_0 - 4\Omega_0\cos\Omega_0)$ or

$$-H_{12} = \left\{ \frac{Q_1}{[4(\tan\Omega_0 - \Omega_0)/\pi + 2]\cos\Omega_0} \right\}^2. \quad (\text{A3})$$

In the other case, if $-\pi < \Omega_0 \leq 0$, Eq. (15) is rewritten

$$2\pi|Q_1| = 2\sqrt{-H_{12}} \left\{ \int_{-\Omega_0}^{2\pi+\Omega_0} (\cos\Omega_0 - \cos\Omega) d\Omega + \int_{2\pi+\Omega_0}^{2\pi-\Omega_0} (\cos\Omega - \cos\Omega_0) d\Omega \right\}.$$

Performing the integration yields

$$2\pi|Q_1| = 2\sqrt{-H_{12}}(-4\sin\Omega_0 + 2\pi\cos\Omega_0 + 4\Omega_0\cos\Omega_0)$$

or

$$-H_{12} = \left\{ \frac{Q_1}{[-4(\tan\Omega_0 - \Omega_0)/\pi + 2]\cos\Omega_0} \right\}^2. \quad (\text{A4})$$

Finally, introducing a parameter \hat{p} with the definition $\hat{p} = \Omega_0$ for $\Omega_0 > 0$ and $\hat{p} = -\Omega_0$ for $\Omega_0 < 0$, Eqs. (A3) and (A4) can be unified so that we arrive at Eq. (18).

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