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Competition between the chiral smectic-*C** and hexatic phases

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A theory of the phase transition from the smectic-C^* to the hexatic phase based on the free energy with the two different Lifshitz terms is presented. Competition between the elastic energies of the tilt angle and of the hexatic order leads either to the single helicoidal structure, or to the double modulated solitonlike structure, and the transformation between both can occur. The bond order and the tilt angle suppress each other and at the transition to the low-temperature hexatic phase a decrease of the tilt angle and an anomaly in the helical pitch occur. Approaching the hexatic phase transition the dielectric response is contributed mainly by the bond-order phason or (and) the tilt angle phason. While the bond-order phason frequency decreases the tilt angle frequency increases in the hexatic phase. Both situations are treated being observed in experiment.

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I. INTRODUCTION

The smectic phases of liquid crystals are layered structures, in which the rodlike molecules are lined up within the smectic layers. In the smectic-*A* (Sm-*A*) phase the molecular axes are on average parallel to the address layer normal, the macroscopic polarization is zero, and the symmetry of this structure is $D_{\infty v}$. At lower temperatures in the Sm-*C* phase the molecules are tilted and the symmetry is lowered to C_{2h}. Further cooling can result in development of hexatic order that is characterized by a long-range three-dimensional bond orientation order (BOO) and a short-range translational order, which extends a few hundred angströms within a smectic layer but one order less between them. It means that crystallographic axes of neighboring smectic layers are parallel (point symmetry exists), but molecules are not translationally correlated (lack of translational symmetry). A hexatic order was first reported in an untilted Sm-B_{hex} phase [1–5] and observed as a diffuse sixfold pattern in an x-ray diffraction [1,2]. In tilted phases the BOO is coupled with the molecular tilt and the local tilt points either along the local bond directions (Sm-*I*), between them (Sm-*F*), or nonsymmetrically (Sm-*L*), see Fig. 1. In contrast with the Sm-B_{hex} phase the sixfold axis is lost in both Sm-*I* and Sm-*F* phases due to the tilt of molecules and their symmetry becomes C_{2h}, the same as that of the Sm-*C* phase. As the symmetry of both smectic-*C* and tilted hexatic phases is the same, there is either a possibility of the first-order transition with a discontinuous change of the orientational order, or a continuous evolution from one phase to the other [6,7].

In the liquid crystals composed of the chiral molecules, the Sm-*A* phase has lower symmetry D_∞. The low-temperature phases of chiral substances (Sm-C^*, Sm-B^*_{hex}, Sm-I^*, Sm-F^*) have analogous local structure as their nonchiral counterparts, but they exhibit helicoidal modulation along the normal of the smectic layers and they all have the same symmetry C_2 [8]. In the Sm-C^* phase the helicoidal modulation of the molecular orientations occurs, in the chiral untilted Sm-B^*_{hex} phase the orientation of intermolecular bonds is modulated, and the spatial variation of both the tilt and the bond orientations exists in the tilted hexatic Sm-I^* and Sm-F^* phases. In the chiral tilted phases the macroscopic polarization exists, which is proportional to the tilt angle.

A model describing the phase sequence Sm-*A*–Sm-*C*–hexatic smectic was developed taking into account a coupling of the tilt and bond orientation [6,7]. Accounting also for modulation of the tilt and bond orientation within the temperature independent model, it was shown that an incommensurate structure can exist in the hexatic phase [9]. The extended theory encountering also the coupling with the polarization was worked out and successfully used for explanation of dielectric spectra observed in ferroelectric chiral phases Sm-C^* and Sm-I^* (or Sm-F^*) in the vicinity of the phase transition to the hexatic phase [10]. This theory describes the softening of the bond orientation mode under the condition that the spatial modulation of the BOO is fully imposed by the tilt angle modulation and the pitch of the helix and the molecular tilt does not change when passing

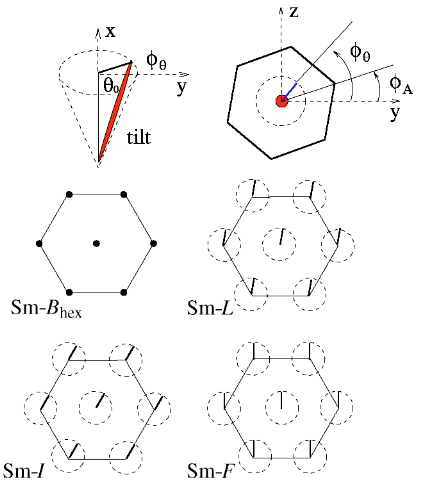

FIG. 1. Structures of hexatic phases; ϕ_A describes the orientation of the bonds, ϕ_θ is the orientation of the director projection to the *yz* plane, θ_0 is the molecular tilt angle with respect to the smectic layer normal.

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the transition point to the hexatic phase. Meanwhile novel ferroelectric substances exhibiting the change of both of the tilt [11] and the pitch at the transition point to the hexatic phase have been reported showing also peculiar temperature dependence of the dielectric spectra. Here we present a theory that generalizes the approach used previously in Ref. [10] encountering also for elastic energy of the BOO modulation. Besides ferroelectric Sm-C^* phase and hexatic Sm-I^* and Sm-F^* phases it allows to obtain also incommensurate and untilted Sm-B^*_{hex} phase.

II. THEORY

A. Order parameters and free energy

There are three quantities playing an essential role in description of the phase transition (PT) sequence Sm-$A(D_\infty)$ $\rightarrow$Sm-$C^*(C_2)\rightarrow$Sm-$I^*(C_2)$ or Sm-$F^*(C_2)$:

$$\theta=\theta_0\exp[i(\phi_\theta+\pi/2)],$$

$$A=A_0\exp[i6\phi_A],$$

$$P=P_0\exp[i\phi_P]. \tag{1}$$

The tilt angle θ describes the inclination of the molecular axis from the smectic layer normal (z axis) and becomes nonzero in the Sm-C^* phase, the bond-order A describes the hexagonal ordering of molecules in the smectic layer, but without appearance of any translation symmetry inside the layer. The bond order becomes essentially nonzero in the hexatic phase, but since the symmetry of the Sm-C^* and hexatic is equal, a weak nonzero BOO appears also in the Sm-C^* phase. Consequently the Sm-$C^*\rightarrow$Sm-I^* (or Sm-F^*) phase transition should be smeared or of the first order. The polarization P is induced by the spontaneous order parameters (OP) or by the external electric field. All three quantities possess an amplitude and a phase, the latter describes rotation around smectic layer normal z axis. The free energy expansion reads

$$F=F_\theta+F_P+F_A+F_{int}, \tag{2}$$

where

$$F_\theta=\frac{1}{2}a(\theta\theta^*)+\frac{1}{4}b(\theta\theta^*)^2+\frac{i}{2}\lambda(\theta\dot{\theta}^*-\dot{\theta}\theta^*)+\frac{1}{2}\kappa(\dot{\theta}\dot{\theta}^*), \tag{3a}$$

$$F_P=\tfrac{1}{2}\chi^{-1}PP^*, \tag{3b}$$

$$F_A=\frac{1}{2}\alpha AA^*+\frac{1}{4}\beta(AA^*)^2+\frac{1}{6}\gamma(AA^*)^2 \\ +\left(\frac{i}{2}\right)\Lambda(A\dot{A}^*-\dot{A}A^*)+\frac{1}{2}K(\dot{A}\dot{A}^*), \tag{3c}$$

$$F_{int}=\tfrac{1}{2}c(P\theta^*+P^*\theta)+\tfrac{1}{2}f(\theta^6A^*+\theta^{*6}A) \\ +\tfrac{1}{2}g(\theta^5PA^*+\theta^{*5}P^*A), \tag{3d}$$

where in the interaction part of the free energy F_{int} the terms higher than linear in P and in A were omitted [10]. The free energy in polar coordinates is

$$F_\theta=\tfrac{1}{2}a\theta_0^2+\tfrac{1}{4}b\theta_0^4+(\lambda\dot{\phi}_\theta+\tfrac{1}{2}\kappa\dot{\phi}_\theta^2)\theta_0^2+\tfrac{1}{2}\kappa\dot{\theta}_0^2, \tag{4a}$$

$$F_P=\tfrac{1}{2}\chi^{-1}P_0^2, \tag{4b}$$

$$F_A=\tfrac{1}{2}\alpha A_0^2+\tfrac{1}{4}\beta A_0^4+\tfrac{1}{6}\gamma A_0^6+(6\Lambda\dot{\phi}_A+\tfrac{1}{2}36K\dot{\phi}_A^2)A_0^2 \\ +\tfrac{1}{2}K\dot{A}_0^2, \tag{4c}$$

$$F_{int}=cP_0\theta_0\cos[\phi_P-\phi_\theta-\pi/2]+f\theta_0^6A_0\cos[6(\phi_\theta-\phi_A \\ +\pi/2)]+g\theta_0^5P_0A_0\cos[5(\phi_\theta+\pi/2)-6\phi_A+\phi_P]. \tag{4d}$$

In the equilibrium the phase and the amplitude of polarization is

$$\phi_P=\phi_\theta\pm\pi/2,$$

$$P_0=\pm\{-\chi c\theta_0-\chi g\theta_0^5A_0\cos[6(\phi_\theta-\phi_A+\pi/2)]\}, \tag{5}$$

where the "+" sign corresponds to $c<0$, and the "−" sign to $c>0$. The polarization is always perpendicular to the tilt and c determines its sense. Further usually we shall consider $c<0$. According to Eq. (5) the polarization can exhibit a change at the transition to the hexatic phase [10]. In any case the reduced free energy reads

$$F_\theta=\tfrac{1}{2}(a-\chi c^2)\theta_0^2+\tfrac{1}{4}b\theta_0^4+(\lambda\dot{\phi}_\theta+\tfrac{1}{2}\kappa\dot{\phi}_\theta^2)\theta_0^2+\tfrac{1}{2}\kappa\dot{\theta}_0^2, \tag{6a}$$

$$F_A=\tfrac{1}{2}\alpha A_0^2+\tfrac{1}{4}\beta A_0^4+\tfrac{1}{6}\gamma A_0^6+(6\Lambda\dot{\phi}_A+\tfrac{1}{2}36K\dot{\phi}_A^2)A_0^2 \\ +\tfrac{1}{2}K\dot{A}_0^2, \tag{6b}$$

$$F_{int}=f_i\theta_0^6A_0\cos[6(\phi_\theta-\phi_A+\pi/2)], \tag{6c}$$

where the interaction constant $f_i\equiv f-\chi cg$. The relation between the tilt angle phase ϕ_θ and BOO phase ϕ_A determines the type of the hexatic phase, and it will be calculated in the next step. For that the interaction constant f_i is the most important parameter.

B. Determination of possible structures

1. Noninteracting helices of tilt and bond orientation

For future references we display here the equilibrium state for the system, in which the tilt and BOO do not interact, $f_i=0$. It consists of two independent helices, the helix of the tilt and of the BOO, respectively,

$$\tilde{\theta}_0^2=a_0(\tilde{T}_C-T)/b,\quad \tilde{T}_C=T_1+(\chi c^2+\kappa q_\theta^2)/a_0,$$

$$\tilde{\phi}_\theta=-q_\theta x+C_\theta,\quad q_\theta=\frac{2\pi}{p_\theta}=\lambda/\kappa,\quad T<\tilde{T}_C \tag{7a}$$

$$\tilde{A}_0^2 \simeq 3|\beta|/4\gamma + \frac{2\alpha_0}{|\beta|}(\tilde{T}_I - T),$$

$$\tilde{T}_I = T_2 + 36Kq_A^2/\alpha_0 + \alpha_0^{-1}3\beta^2/16\gamma,$$

$$\tilde{\phi}_A = -q_A x + C_A, \quad q_A = \frac{2\pi}{p_A} = 6\Lambda/36K, \quad T < \tilde{T}_I, \tag{7b}$$

where the tilde denotes the equilibrium values for this noninteracting case, $\tilde{T}_C$, p_θ are the phase transition temperature and pitch of helix for the Sm-C^* phase, and likewise for the hexatic phase. The tilt angle and BOO helices should have the same chirality sense [12], and therefore $\lambda > 0$, $\Lambda > 0$ are considered in the following. In accordance with our preliminary experimental finding we assume further that $q_\theta < q_A$ and that Sm-C^* phase appears at higher temperature than the hexatic order, i.e., $\tilde{T}_I < \tilde{T}_C$. In the Sm-$A$ phase both the tilt and the BOO are zero. In the Sm-C^* phase tilt is determined by Eq. (7a) and BOO is still exactly zero. In the hexatic phase there are two independent helices (7) with the pitch p_θ and p_A, and their phases are not related. In such a case the Sm-I^* structure defined as (see Fig. 1)

$$\phi_A = \phi_\theta + n\frac{\pi}{3}, \quad n = 0, \ldots, 5, \tag{8}$$

the SmF^* structure defined as

$$\phi_A = \phi_\theta + \frac{\pi}{6} + n\frac{\pi}{3}, \quad n = 0, \ldots, 5, \tag{9}$$

and the structure Sm-L of the lowest symmetry C_1, in which the bond orientation ϕ_A and the orientation of the tilt ϕ_θ do not fulfill relations (8) or (9), are energetically degenerated. The hexatic phases Sm-I^* or Sm-F^* become stable when the interaction between the tilt and BOO is switched on. In each of the hexatic phases [Sm-I^* (8) and Sm-F^* (9)] there are six equivalent configurations.

2. Sinusoidal and solitonlike structures

Let us encounter the interaction between the tilt and BOO, i.e., $f_i \neq 0$. For simplicity, in the following the amplitudes θ_0 and A_0 are assumed being constant and they will be determined later. This assumption is exact when the phases are linear functions of the space coordinate z, while it is a constant amplitude approximation for more complicated spatial variation. The equilibrium phases follow from the free energy minimization and the corresponding Lagrange-Euler equations read

$$\theta_0^2\kappa\ddot{\phi}_\theta + 36A_0^2K\ddot{\phi}_A = 0, \tag{10a}$$

$$6A_0\kappa K(\ddot{\phi}_\theta - \ddot{\phi}_A) = -f_i\theta_0^4(36A_0^2K + \theta_0^2\kappa) \times \sin[6(\phi_\theta - \phi_A + \pi/2)]. \tag{10b}$$

Let us first consider $f_i > 0$. There are two possible solutions. The first one represents the Sm-I^* phase and reads

$$\phi_\theta = \phi_A = -q\,x + \phi_0, \tag{11}$$

where ϕ_0 is arbitrary and q should be determined [we chose $n=0$ in Eq. (8)]. It means that the structure has a single sinusoidal modulation. The second solution represents an incommensurate structure [13]

$$\phi_\theta = \frac{\sigma^2}{(1+\sigma^2)}\left(\pm\frac{1}{3}\mathrm{am}\left[\frac{\sqrt{(1+\sigma^2)/\rho}}{k}(x-x_0)\middle| k\right] - \frac{\pi}{2}\right) - qx + \phi_0, \tag{12a}$$

$$\phi_A = \frac{1}{(1+\sigma^2)}\left(\mp\frac{1}{3}\mathrm{am}\left[\frac{\sqrt{(1+\sigma^2)/\rho}}{k}(x-x_0)\middle| k\right] + \frac{\pi}{2}\right) - qx + \phi_0, \tag{12b}$$

with dimensionless quatities

$$\sigma^2 \equiv \frac{36A_0^2K}{\theta_0^2\kappa}, \quad \rho \equiv \frac{A_0K}{f_i\theta_0^6}, \tag{13}$$

and it only exists when modulus $k \leqslant 1$. For $k=1$ solutions (11) and (12) coincide. The quantities ϕ_0, q, x_0, and k are integration constants that should be determined. For that purpose solution (12) is inserted to Eq. (6) and integrating over all the space the total free energy (per unit volume) is obtained:

$$F_{\mathrm{tot}} = \frac{1}{2}(a-\chi c^2)\theta_0^2 + \frac{1}{4}b\theta_0^4 + \frac{1}{2}\alpha A_0^2 + \frac{1}{4}\beta A_0^4 + \frac{1}{6}\gamma A_0^6 + \frac{1}{2}(\kappa\theta_0^2 + 36KA_0^2)q^2 - (\lambda\theta_0^2 + 6\Lambda A_0^2)q + f_iA_0\theta_0^6\left\{1 + 2\left[\frac{2}{k^2}\left(\frac{\mathbf{E}[k]}{\mathbf{K}[k]} - 1\right) + \frac{1}{k^2} \pm \frac{\nu}{\mathbf{K}[k]k}\right]\right\}, \tag{14a}$$

$$\nu = 3\pi\sqrt{\rho/(1+\sigma^2)}|q_\theta - q_A| = \nu_0\sqrt{\frac{2\sigma}{1+\sigma^2}}, \tag{14b}$$

where ν is a dimensionless parameter,

$$\nu_0^2 = \frac{9\pi^2\sqrt{K\kappa}}{12f_i\theta_0^5}(q_A - q_\theta)^2$$

is independent of A_0, and σ linearly depends on A_0. The phase ϕ_0 and the position x_0 are arbitrary and the values of q and k should be found from the free energy minimum. Note that q and k are explicitly decoupled. For the equilibrium q,

$$q = \frac{\lambda\theta_0^2 + 6\Lambda A_0^2}{\kappa\theta_0^2 + 36KA_0^2}, \quad q_\theta \leqslant q \leqslant q_A. \tag{15}$$

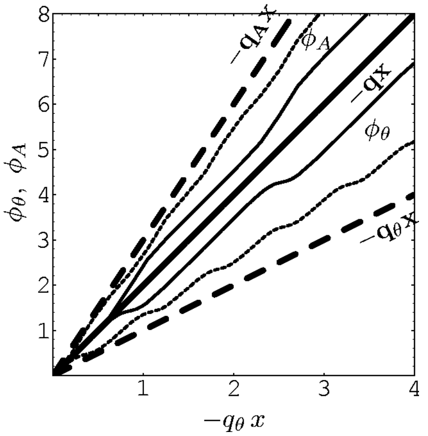

FIG. 2. Spatial dependence of tilt and BOO phases (full bold line). The hexatic Sm-I^* phase with $\phi_\theta=\phi_A=-q\,x$ (full lines); the phases ϕ_θ and ϕ_A according to Eq. (12) for $1-k=10^{-6}$ (dotted lines); for $1-k=10^{-2}$ (dashed bold lines); independent helices for $k=0$. The parameters used are $q_A/q_\theta=3$ and $\sigma=1$.

The equilibrium value of modulus k is independent of q vector and can be obtained by setting to zero the derivation of the free energy (14a) with respect to k (it can be shown that the sign "$-$" corresponds to the minimum). The modulus k cannot be expressed explicitly, but it is a solution of the equation

$$2\mathbf{E}[k]-\nu k=0$$

$$\text{for}\quad \nu>2[\text{incommensurate structure}(12),\quad k<1], \tag{16a}$$

$$k=1\quad\text{for}\quad \nu\leqslant 2\ \ [\text{Sm-}I^*\text{structure}(11)]. \tag{16b}$$

Let us discuss the structures described by solutions (11), (12), (15), and (16). They depend on the parameter ν.

The strong interaction regime occurs for $\nu\leqslant 2$. Then the Sm-I^* phase (11) with q vector (15) is a stable structure, the cosine in the interaction part of the free energy (6c) being exactly -1 (see Fig. 2).

For $\nu>2$ (the weak interaction regime), incommensurate structure (12) occurs. It is represented by the array of solitons for $\nu\gtrsim 2$ (then $k\lesssim 1$). Then the Sm-I^* domains (8) of the size $d=2\mathrm{K}[k]\approx 2\ \ln[4/\sqrt{1-k^2}]$ are separated by kinks (discommensurations). Each kink produces $\pi/3$ phase difference and the full rotation of the tilt with respect to BOO is accomplished by six kinks (see Figs. 2 and 3).

In the limit $\nu\gg 2$, the modulus $k\approx\pi/\nu\ll 1$, and the structure consists of two weakly interacting sinusoidal modulations, of the tilt angle with $\dot{\phi}_\theta=-q_\theta$ and of the bond order with $\dot{\phi}_A=-q_A$. When $k=0$, the spatial average of the interaction part of free energy (6c) is zero. Then two independent helices described by Eq. (7) are obtained, which can slide independently.

Finally, the arbitrary phase ϕ_0 in Eq. (12) describes the position of the underlying helix with q vector [see also Eq. (8)], and the arbitrary coordinate x_0 in Eq. (12) describes the position of a periodic kink superstructure. Henceforth, there are two Goldstone modes in the incommensurate phase (12), while there is only one Goldstone mode in the sinusoidal structure (11).

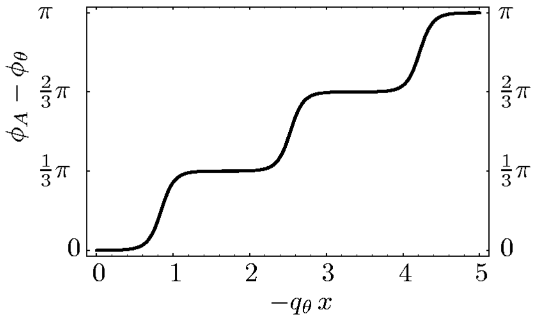

FIG. 3. Spatial dependence of the difference $\phi_A-\phi_\theta$ in the incommensurate structure for the same parameters as in Fig. 2 and for $1-k=10^{-6}$.

In Fig. 4 the control parameter ν is plotted versus σ according to Eq. (14b). Since $\sigma\propto A_0$, and A_0 increases when crossing the phase transition from the Sm-C^* to the hexatic phase, the figure also qualitatively shows the temperature behavior of ν. The incommensurate structure can appear if $\nu>2$, which could happen in a finite temperature interval near the hexatic phase transition. The nature of the control parameter ν can be elucidated writting it in the form

$$\nu^2=\frac{\pi^2}{2}\,\frac{W_{el}}{W_{int}}, \tag{17}$$

where $W_{el}^{-1}=W_\theta^{-1}+W_A^{-1}$, $W_\theta=\frac{1}{2}\kappa\theta_0^2(q_\theta-q_A)^2$, $W_A=\frac{1}{2}36KA_0^2(q_\theta-q_A)^2$. W_θ is an energy increase when the modulation of the tilt angle is shrunk from $2\pi/q_\theta$ to $2\pi/q_A$ [calculated from Eq. (6a)], and likewise W_A represents energy increase when the modulation of BOO is stretched from $2\pi/q_A$ to $2\pi/q_\theta$ [calculated from Eq. (6b)]. When matching both helices W_{el} represents a characteristic increase of elastic energy and $W_{int}=f_i\theta_0^6A_0$ is an energy gain coming from the interaction between the tilt and BOO. The sinusoidal structure (Sm-I^*) appears when the interaction energy is larger than the elastic one, while for much higher elastic energy as

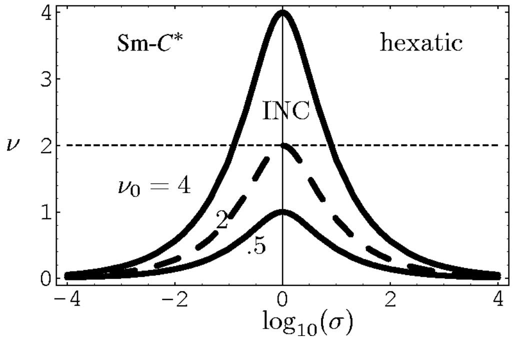

FIG. 4. Dependence of parameter ν on σ according to Eq. (14b). Since σ is proportional to BOO amplitude A_0, which increases when crossing the transition point to the hexatic phase, the incommensurate structure could exist in a finite temperature range when $\nu>2$.

compared with the interaction energy, the solitonlike structure or two nearly independent helices exist.

C. Equilibrium values of the tilt angle and BOO amplitudes

The control parameter ν and the structural parameters q vector and the modulus k depend on the amplitudes A_0 and θ_0, which are still not determined. For the sake of simplicity and also due to the fact that the incommensurate regime could, if ever, exist within a finite temperature interval, further we consider the sinusoidal structure only (Sm-I^* phase). The corresponding free energy

$$F_{tot}=\tfrac{1}{2}(a-\chi c^2-\kappa q^2)\theta_0^2+\tfrac{1}{4}b\theta_0^4+\tfrac{1}{2}(\alpha-36Kq^2)A_0^2 + \tfrac{1}{4}\beta A_0^4+\tfrac{1}{6}\gamma A_0^6-f_iA_0\theta_0^6, \tag{18}$$

where the equilibrium value (15) of q is a function of two variables θ_0 and A_0. It is convenient to introduce dimensionless normalized quantities:

$$X=\frac{\theta_0}{\tilde{\theta}_0},\quad Y^2=\frac{36KA_0^2}{\kappa\tilde{\theta}_0^2}, \tag{19a}$$

$$\Delta^2=\frac{\kappa}{b\tilde{\theta}_0^2}(q_A-q_\theta)^2,\quad \tilde{\alpha}=(\alpha-36Kq_A^2)\frac{\kappa}{b\tilde{\theta}_0^2 36K},$$

$$\tilde{\beta}=\frac{\beta\kappa^2}{b(36K)^2},\quad \tilde{\gamma}=\frac{\gamma\tilde{\theta}_0^2\kappa^3}{b(36K)^3},$$

$$\tilde{f}_i=f_i\frac{\tilde{\theta}_0^3}{b}\sqrt{\frac{\kappa}{36K}}, \tag{19b}$$

where $\tilde{\theta}_0$ is defined in Eq. (7a). The normalized BOO Y is similar to the quantity σ [defined in Eq. (13)] and they are related as $Y=\sigma X$. When there is no coupling between the tilt and BOO, then the tilt $\theta_0=\tilde{\theta}_0$ does not dependent on A_0 and $X=1$ [see Eqs. (19a) and (7a)]. Deviation of X from 1 can appear only for nonzero interaction, $f_i\neq 0$. The wave vector (15) can be rewritten as

$$q=\frac{X^2q_\theta+Y^2q_A}{X^2+Y^2}, \tag{20}$$

and the normalized free energy $\tilde{F}_{tot}$ is

$$\tilde{F}_{tot}=\frac{F_{tot}}{b\tilde{\theta}_0^4}=-\frac{1}{2}X^2+\frac{1}{4}X^4+\frac{\tilde{\alpha}}{2}Y^2+\frac{\tilde{\beta}}{4}Y^4+\frac{\tilde{\gamma}}{6}Y^6 +\frac{\Delta^2}{2}\frac{X^2Y^2}{X^2+Y^2}-\tilde{f}_iYX^6. \tag{21}$$

The interaction term is negative and the stability condition requires positive tilt angle expansion terms up to the 12th order. Considering the free energy up to the fourth power of the tilt only, the interaction term has to be neglected while searching for the equilibrium value of the tilt. On the other hand the interaction term is linear in Y, and therefore it should be preserved when finding the BOO equilibrium value. The extremes of the free energy are solutions of the equations

$$X\left((-1+X^2)+\frac{Y^4}{(X^2+Y^2)^2}\Delta^2\right) =X\left((-1+X^2)+\frac{\kappa}{b\tilde{\theta}_0}(q-q_\theta)^2\right)=0, \tag{22a}$$

$$-\tilde{f}_iX^6+Y\left((\tilde{\alpha}^o+Y^2)\tilde{\beta}+\frac{X^4}{(X^2+Y^2)^2}\Delta^2\right) =-\tilde{f}_iX^6+Y\left((\tilde{\alpha}^o+Y^2)\tilde{\beta}+\frac{\kappa}{b\tilde{\theta}_0}(q-q_A)^2\right)=0, \tag{22b}$$

where $\tilde{\alpha}^o=\tilde{\alpha}/\tilde{\beta}$. Two variations of the left sides are shown for convenience.

1. Relation of the tilt and the bond order

The equilibrium state is a solution of Eqs. (22). Inspecting dependence of the tilt on the BOO, absolute and local minima (with respect to X and at fixed Y) should be determined using Eqs. (22a) and (21). It leads to the phase diagram in the (Δ, Y) plane, exhibiting the tilted hexatic Sm-I^* phase (region with $X>0$, $Y>0$) and the untilted hexatic Sm-B^*_{hex} phase ($X=0$, $Y>0$), see Fig. 5. The line of the phase transitions between the both phases (figure) consists of two parts: the first-order PT line in the (Δ,Y) plane

$$\Delta^2=\frac{(2+Y^2)^2}{8Y^2},\quad 0<Y^2<2\quad(\Delta^2>1) \tag{23}$$

that ends at the critical point $\Delta^2=1$, $Y^2=2$, and the straight line of the second-order PT's

$$\Delta^2=1,\quad Y^2>2. \tag{24}$$

The metastability line of the tilted hexatic Sm-I^* phase is

$$\Delta^2=\frac{4(1+Y^2)^3}{27Y^4},\quad 0<Y^2<2,$$

and the metastability region of the Sm-B^*_{hex} is

$$1<\Delta^2<\frac{(2+Y^2)^2}{8Y^2},\quad 0<Y^2<2.$$

Note that the Y^2 axis is directed to the left in Fig. 5. It is convenient to show schematically also the temperature axis. For that purpose we assume Landau-like temperature behavior of the BOO: $Y^2=0$, for $T>T_I$, $Y^2\propto(T_I-T)$ for $T<T_I$ [The exact behavior of $Y(T)$ can be obtained from Eqs. (22)], in reality it exhibits a jump at T_I, see below). For $T>T_I$ the Sm-C^* phase exists, in which $X>0$ and $Y=0$. The cooling process of the sample is represented by a horizontal

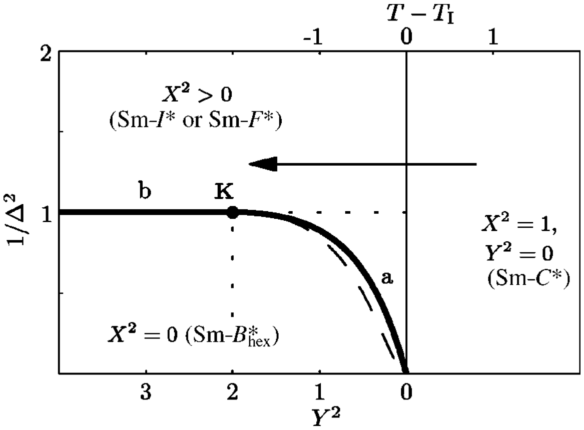

FIG. 5. The phase diagram in the (Δ, Y) plane; the PT points of the first order (line *a*), the PT points of the second order (line *b*), the critical point *K*. The dashed line denotes metastability of the hexatic tilted phase. For $T > T_I$, $Y=0$. The arrow shows a path when cooling the sample. Depending on the value of Δ the tilted or untilted hexatic phase can occur below T_I. The schematically shown temperature axis is in arbitrary units.

path in the phase diagram and the arrow in Fig. 5 is an example. It means that on cooling the sequence, Sm-$C^* \rightarrow$Sm-I^* or Sm-$C^* \rightarrow$Sm-$I^* \rightarrow$Sm-B^*_{hex} can appear depending on the value of Δ. One should realize that continuous variation of BOO parameter Y is assumed above, but due to the first-order PT the jump up of Y occurs at T_I. Therefore the Sm-$C^* \rightarrow$Sm-B^*_{hex} transition can also occur.

On the basis of Eq. (22a) the tilt X as a function of the bond-order Y can be calculated. The results are shown for several values of Δ in Fig. 6. In order to see the temperature dependence of the tilt angle, we introduce schematically the temperature axis in Fig. 6. There is always a decrease of the tilt caused by the appearance of the BOO. In the hexatic phase the tilt, depending on the value of Δ, can remain nonzero (path does not cross the line *a* in Fig. 5) or it can drop down to zero value (the path crosses line *a*). The latter case corresponds to the first-order phase transition from Sm-I^* phase to the untilted Sm-B^*_{hex} phase. For $\Delta^2<1$ the equation for the tilt can be written as $X^2=1-\Delta^2 Y^4/(X^2+Y^2)^2$, or

$$X^2=1-\frac{\kappa}{b\tilde{\theta}_0}(q-q_\theta)^2. \tag{25}$$

Equation (25) is implicit since the q vector itself depends on X, see Eq. (20). In the Sm-C^* phase $Y\approx 0$ and then $q\approx q_\theta$ and $X\approx 1$. In the hexatic phase $Y>0$, then $q>q_\theta$ and $X<1$. For large A_0 the q vector approaches q_A and the tilt saturates at the value of $X^2=1-(\kappa/b\tilde{\theta}_0)(q_A-q_\theta)^2$. Summarizing, when crossing the PT to the hexatic phase the increase of BOO causes variation of the q vector (its deviation from q_θ) and consequently it results in the decrease of the tilt angle.

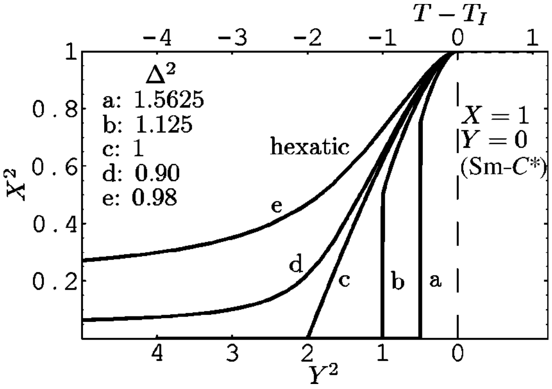

FIG. 6. Dependence of the normalized tilt X on the BOO Y. The tilt decreases when BOO increases below T_I. The first-order phase transition from Sm-I^* to Sm-B^*_{hex} occurs when $\Delta>1$ (curves *a* and *b*). The marginal behavior for $\Delta=1$ (curve *c*). For $\Delta<1$ the tilt saturates at a nonzero value and the system remains in the Sm-I^* phase at low temperatures. The temperature axis (arbitrary units) is shown schematically.

2. The bond-order temperature behavior

The dependence of the BOO on the temperature follows from Eq. (22b). The transition to the hexatic phase is of the first order and the nonzero, even if very small, BOO exists also in the Sm-C^* phase. Since in the Sm-C^* is $\theta_0\approx\tilde{\theta}_0$, $Y\ll 1$ and $q\approx q_\theta$, the BOO can be expressed as

$$Y=\sqrt{\frac{36KA_0^2}{\kappa\tilde{\theta}_0^2}}\approx\frac{f_i\tilde{\theta}_0^5\sqrt{36K/\kappa}}{\alpha_0(T-\tilde{T}_2)}\ll 1, \quad T>T_I, \tag{26}$$

where $\tilde{T}_2=T_2+\alpha_0^{-1}36K[q_A^2-(q_A-q_\theta)^2]$. The hexatic phase transition temperature T_I can be obtained in the form

$$T_I=T_2+\alpha_0^{-1}36K(q_A^2-(q_A-q)^2)+\alpha_0^{-1}3\beta^2/16\gamma, \tag{27}$$

where q depends on the BOO amplitude A_0 [see Eq. (15) or Eq. (20)], and A_0 is determined by the implicit expression

$$A_0^2=\frac{-\beta+\sqrt{\beta^2-4\gamma(\alpha-36K[q_A^2-(q_A-q)^2])}}{2\gamma}, \quad T<T_I. \tag{28}$$

Not far below T_I the BOO can be expressed as

$$A_0^2\simeq 3|\beta|/4\gamma+\frac{2\alpha_0}{|\beta|}(T_I-T), \quad T<T_I. \tag{29}$$

Expressions (27)–(29) were obtained under the assumption that $\tilde{f}_i X^6$ term in Eq. (22b) can be neglected below T_I. The PT temperature T_I as such depends on temperature T [via q and A_0, see Eqs. (15), (27), (28)], which can modify linear temperature dependence (29). In a particular case of noncompeting helices, i.e., when $q_A=q_\vartheta$, the temperature $T_I=T_2+\alpha_0^{-1}36Kq_A^2+\alpha_0^{-1}3\beta^2/16\gamma$ is in agreement with Eq.

(7b). The same value of the PT temperature is obtained for the large values of A_0, when $Y \gg X$ (note that it implies $q \approx q_A$).

III. DYNAMICS

For the dynamic dielectric response we shall proceed in the usual way [10]. First we need the variation of the free energy F caused by small fluctuations around an equilibrium state, $P = P_S + p$, $\theta = \theta_S + \vartheta$, $A = A_S + e$, where

$$p = \delta(P_0 \exp(\mathrm{i}\phi_P)) = (\delta P_0 + \mathrm{i}\delta\phi_P P_0)\exp[\mathrm{i}\phi_P]$$

$$= (p_1 + \mathrm{i}p_2)\exp[\mathrm{i}\phi_P],$$

$$\vartheta = (\vartheta_1 + \mathrm{i}\vartheta_2)\exp[\mathrm{i}(\phi_\theta + \pi/2)],$$

$$e = (e_1 + \mathrm{i}e_2)\exp[\mathrm{i}6\phi_A], \tag{30}$$

p_1 is the fluctuation of the amplitude (amplitudon), and p_2 is the fluctuation of the phase (phason) of the polarization. Likewise we have amplitudon ϑ_1 and phason ϑ_2 of the tilt and amplitudon e_1 and phason e_2 of the bond orientation. In case of $\nu > 2$ the incommensurate equilibrium structure exists in a finite temperature interval. We restrict further analysis for the simple case $\nu < 2$ when a single helical structure with wave vector (15) exists in the whole temperature range. Then the (second) variation of free energy (2) reads

$$\begin{aligned}\delta F = {} & \frac{1}{2}(a + 3b\theta_0^2 + 2\lambda\dot{\phi}_\theta + \kappa\dot{\phi}_\theta^2)\vartheta_1^2 + \frac{1}{2}(a + b\theta_0^2 + 2\lambda\dot{\phi}_\theta \\ & + \kappa\dot{\phi}_\theta^2)\vartheta_2^2 + \frac{\kappa}{2}(\dot{\vartheta}_1^2 + \dot{\vartheta}_2^2) + (\lambda + \kappa\dot{\phi}_\theta)(\vartheta_1\dot{\vartheta}_2 - \dot{\vartheta}_1\vartheta_2) \\ & + \frac{1}{2}[\alpha + 3\beta A_0^2 + 2(6\Lambda)\dot{\phi}_A + 36K\dot{\phi}_A^2]e_1^2 + \frac{1}{2}[\alpha + \beta A_0^2 \\ & + 2(6\Lambda)\dot{\phi}_A + 36K\dot{\phi}_A^2]e_2^2 + \frac{36K}{2}(\dot{e}_1^2 + \dot{e}_2^2) \\ & + (\Lambda + 6K\dot{\phi}_A)(e_1\dot{e}_2 - \dot{e}_1 e_2) + \frac{1}{2}\chi^{-1}(p_1^2 + p_2^2) \\ & - c(\vartheta_1 p_1 + \vartheta_2 p_2) \mp [10g\theta_0^3 P_0 A_0(\vartheta_1^2 - \vartheta_2^2) \\ & + g\theta_0^5(p_1 e_1 + p_2 e_2)] - \frac{1}{2}(p + p^*)E_x,\end{aligned} \tag{31}$$

where we put $f = 0$ for simplicity, and also we omitted terms $5g\theta_0^4 A_0(\vartheta_1 p_1 - \vartheta_2 p_2)$, $5g\theta_0^4 P_0(\vartheta_1 e_1 + \vartheta_2 e_2)$, i.e., among the g terms only bilinear coupling between the polarization and the bond-order fluctuations, and the local potential terms proportional to ϑ_1^2 and ϑ_2^2 are kept. These simplifications do not change the results qualitatively. The $+$ sign corresponds to $f_i = -\chi c g < 0$ and appearance of the Sm-*F** phase, the $-$ sign is for $f_i = -\chi c g > 0$ and the Sm-*I** phase. In the following we will treat only the case $f_i > 0$ [with $c < 0$, $g > 0$, see Eq. (5)] corresponding to the Sm-*I** phase. On the basis of the Landau-Khalatnikov relaxation equations the dynamical equations can be derived as

$$-E_0\sin(qz) = (\chi^{-1} + i\omega\gamma_{p1})p_1 - c\vartheta_1 - g\theta_0^5 e_1,$$

$$\begin{aligned}0 = {} & -\kappa\ddot{\vartheta}_1 - 2\kappa\Delta_\theta\dot{\vartheta}_2 + (a + 3b\theta_0^2 - \lambda^2/\kappa + \kappa\Delta_\theta^2 \\ & - 10\chi|c|g\theta_0^4 A_0)\vartheta_1 - cp_1,\end{aligned}$$

$$\begin{aligned}0 = {} & -36K\ddot{e}_1 - 12K\Delta_A\dot{e}_2 + (\alpha + 3\beta A_0^2 + 5\gamma A_0^4 - \Lambda^2/K \\ & + 36K\Delta_A^2 + i\omega\gamma_{e1})e_1 - g\theta_0^5 p_1,\end{aligned}$$

$$-E_0\cos(qz) = (\chi^{-1} + i\omega\gamma_{p2})p_2 - c\vartheta_2 - g\theta_0^5 e_2,$$

$$\begin{aligned}0 = {} & -\kappa\ddot{\vartheta}_2 + 2\kappa\Delta_\theta\dot{\vartheta}_1 + (a + b\theta_0^2 - \lambda^2/\kappa + \kappa\Delta_\theta^2 \\ & + 10\chi|c|g\theta_0^4 A_0)\vartheta_2 - cp_2,\end{aligned}$$

$$\begin{aligned}0 = {} & -36K\ddot{e}_2 + 12K\Delta_A\dot{e}_1 + (\alpha + \beta A_0^2 + \gamma A_0^4 - \Lambda^2/K + 36K\Delta_A^2 \\ & + i\omega\gamma_{e2})e_2 - g\theta_0^5 p_2,\end{aligned} \tag{32}$$

where $\Delta_\theta \equiv q_\theta - q$, $\Delta_A \equiv q_A - q$, six viscosities γ_{p1}, γ_{p2}, $\gamma_{\vartheta 1}$, $\gamma_{\vartheta 2}$, γ_{e1}, γ_{e2} of corresponding quantities were introduced, and ω is a frequency of homogeneous electric field $E = E_0\exp(i\omega t)$. The solution can be found in the form

$$p_1 = p_{10}\sin qz, \quad \vartheta_1 = \vartheta_{10}\sin qz, \quad e_1 = e_{10}\sin qz,$$

$$p_2 = p_{20}\cos qz, \quad \vartheta_2 = \vartheta_{20}\cos qz, \quad e_2 = e_{20}\cos qz,$$

and Eqs. (32) reduce to

$$\begin{pmatrix} \chi_{p1}^{-1} & -c & -g\theta_0^5 & 0 & 0 & 0 \\ -c & \chi_{\vartheta 1}^{-1} & 0 & 0 & \tilde{\Delta}_\theta & 0 \\ -g\theta_0^5 & 0 & \chi_{e1}^{-1} & \tilde{\Delta}_A & 0 & 0 \\ 0 & 0 & \tilde{\Delta}_A & \chi_{e2}^{-1} & 0 & -g\theta_0^5 \\ 0 & \tilde{\Delta}_\theta & 0 & 0 & \chi_{\vartheta 2}^{-1} & -c \\ 0 & 0 & 0 & -g\theta_0^5 & -c & \chi_{p2}^{-1} \end{pmatrix} \begin{pmatrix} p_{10} \\ \vartheta_{10} \\ e_{10} \\ e_{20} \\ \vartheta_{20} \\ p_{20} \end{pmatrix} = \begin{pmatrix} -E_0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -E_0 \end{pmatrix} \tag{33}$$

where $\tilde{\Delta}_A \equiv 12Kq\Delta_A = 12K(q_A - q)q$, $\tilde{\Delta}_\theta \equiv 2\kappa q \Delta_\theta = 2\kappa(q_\theta - q)q$, and the bare inverse susceptibilities and relaxation times are

$$\chi_{p1}^{-1} = \chi^{-1}(1 + i\omega\tau_{p1}), \quad \tau_{p1} = \gamma_{p1}\chi,$$

$$\chi_{p2}^{-1} = \chi^{-1}(1 + i\omega\tau_{p2}), \quad \tau_{p2} = \gamma_{p2}\chi,$$

$$\chi_{e1}^{-1} = \chi_{e1,0}^{-1}(1 + i\omega\tau_{e1}), \quad \tau_{e1} = \gamma_{e1}\chi_{e1,0},$$

$$\chi_{e1,0}^{-1} = \alpha + 3\beta A_0^2 + 5\gamma A_0^4 + 36K\Delta_A^2,$$

$$\chi_{e2}^{-1} = \chi_{e2,0}^{-1}(1 + i\omega\tau_{e2}), \quad \tau_{e2} = \gamma_{e2}\chi_{e2,0},$$

$$\chi_{e2,0}^{-1} = \alpha + \beta A_0^2 + \gamma A_0^4 + 36K\Delta_A^2,$$

$$\chi_{\vartheta 1}^{-1} = \chi_{\vartheta 1,0}^{-1}(1 + i\omega\tau_{\vartheta 1}), \quad \tau_{\vartheta 1} = \gamma_{\vartheta 1}\chi_{\vartheta 1,0},$$

$$\chi_{\vartheta 1,0}^{-1} = a + 3b\theta_0^2 + \kappa\Delta_\theta^2 - 10\chi|c|g\theta_0^4 A_0,$$

$$\chi_{\vartheta 2}^{-1} = \chi_{\vartheta 2,0}^{-1}(1 + i\omega\tau_{\vartheta 2}), \quad \tau_{\vartheta 2} = \gamma_{\vartheta 2}\chi_{\vartheta 2,0},$$

$$\chi_{\vartheta 2,0}^{-1} = a + b\theta_0^2 + \kappa\Delta_\theta^2 + 10\chi|c|g\theta_0^4 A_0. \tag{34}$$

A. Relaxation frequencies

There are six modes: Three coupled amplitudons p_1, ϑ_1, e_1 and three coupled phasons p_2, ϑ_2, e_2. There is no coupling between phasons and amplitudons of different quantities, but there is a coupling between the phason and amplitudon of the same quantities (ϑ_1, ϑ_2 and e_1, e_2) represented by $\tilde{\Delta}_\theta$ and $\tilde{\Delta}_A$, respectively. Dispersion of the bare polarization modes connected with the rotational motion of molecules along their long axis can be neglected, since they exhibit high frequencies as compare with the tilt and BOO modes (and frequency window of experiment), i.e., $\omega\tau_{pi} \approx 0$, $i = 1$, 2, and $\chi_{pi}^{-1} = \chi^{-1}$. The amplitudon and phason of the tilt are related to the fluctuations of the tilt angle and the rotation of the molecules on the cone, respectively. These motions are of diffusive nature keeping the molecular mass center immobile. The amplitudon and phason of bond order are the slowest modes, since they are related to the diffusive motion of the whole molecules (molecular mass centers). Using Eqs. (22), which determine the equilibrium amplitudes θ_0 and A_0, the bare relaxation frequencies of the tilt and BOO above and below T_I can be expressed as

$$\gamma_{\vartheta 1}\tau_{\vartheta 1}^{-1} = \begin{cases} 2b\theta_0^2 + \kappa q_\theta^2 + \chi c^2, & T > T_I \\ 2b\theta_0^2 + \kappa q_\theta^2 + \chi c^2 - 10\chi|c|g\theta_0^4 A_0, & T < T_I, \end{cases} \tag{35a}$$

$$\gamma_{\vartheta 2}\tau_{\vartheta 2}^{-1} = \begin{cases} \kappa q_\theta^2 + \chi c^2, & T > T_I \\ \kappa q_\theta^2 + \chi c^2 + 10\chi|c|g\theta_0^4 A_0, & T < T_I, \end{cases} \tag{35b}$$

$$\gamma_{e1}\tau_{e1}^{-1} = \begin{cases} \alpha_0(T - T_2) + 36K(q_A - q_\theta)^2, & T > T_I \\ 3\beta^2/4\gamma + 8\alpha_0(T_I - T) + 36Kq_A^2, & T < T_I, \end{cases} \tag{35c}$$

$$\gamma_{e2}\tau_{e2}^{-1} = \begin{cases} \alpha_0(T - T_2) + 36K(q_A - q_\theta)^2, & T > T_I \\ 36Kq_A^2, & T < T_I. \end{cases} \tag{35d}$$

Assuming saturation (or only small temperature variation) of θ_0 far below T_C bare phason (35b) and amplitudon (35a) of the tilt are temperature independent in the Sm-C^* phase. Below T_I, a decrease of the amplitudon frequency and an increase of the phason frequency take place. The latter can be understood realizing that at T_I the hexatic order condenses and creates a local hexagonal potential, which increases the restoring force for the molecular rotation [14]. This effect is one of the candidates for explanation of observed data as will be discussed in the following section.

The bare relaxation frequencies τ_{e1}^{-1} and τ_{e2}^{-1} are equal in the Sm-C^* phase and they soften approaching T_I, while splitting occurs below T_I, see Eqs. (35c) and (35d). At T_I the BOO amplitudon exhibits a jump of

$$9\beta^2/16\gamma - 36K[(q_A - q_\theta)^2 - (q_A - q)^2];$$

for noncompeting helices when $q = q_\theta = q_A$, the jump is $9\beta^2/16\gamma$. The BOO phason decreases of

$$-3\beta^2/16\gamma - 36K[(q_A - q_\theta)^2 - (q_A - q)^2] < 0$$

(for $q = q_\theta = q_A$ it is $-3\beta^2/16\gamma$). The gap between e_1 and e_2 increases from 0 in the Sm-C^* to $3\beta^2/4\gamma$ in the hexatic phase independently of the change of q. The tilt and BOO phasons described above should mainly contribute to the dielectric spectra.

The coupling constants c, g, f cause bindings between different amplitudons and, separately, between phasons and the eigenmodes are actually hybrids of polarization, tilt, and BOO. Due to the coupling c of the fast polarization modes with the slower tilt modes the positive term χc^2 disappears in Eqs. (35a) and (35b), and the lower relaxation frequencies of the Sm-C^* phase are obtained. Due to the coupling $g\theta_0^5$ of polarization, tilt, and BOO, corrections of relaxation frequencies controlled by $g^2\theta_0^{10}$ arise [10], so that τ_{e1} and τ_{e2} slightly differ even in the Sm-C^* phase. Since these corrections do not influence the basic temperature behavior, we neglect them in the following. The remaining coupling parameters $\tilde{\Delta}_A$ and $\tilde{\Delta}_\vartheta$ in Eq. (33) are nonzero if the equilibrium q vector differs from q_A and q_θ, respectively. Then the helix of the tilt and the helix of BOO are deformed, and the coupling of amplitudon e_1 with phason e_2, and coupling of ϑ_1 with ϑ_2 appear. The interaction parameters $\tilde{\Delta}_A$ and $\tilde{\Delta}_\vartheta$

can influence temperature behavior of the relaxation frequencies. The interaction of amplitudon e_1 with phason e_2 via the coupling $\tilde{\Delta}_A$ results in additional shifts of relaxation frequencies. The qualitative behavior can be obtained considering 2×2 matrix inside the dotted frame of Eq. (33). The shifted relaxation frequencies $1/\tau_{e+}$ and $1/\tau_{e-}$ are

$$\tau_{e\pm}^{-1}=\frac{1}{2}\left(\tau_{e1}^{-1}+\tau_{e2}^{-1}\pm\sqrt{(\tau_{e1}^{-1}-\tau_{e2}^{-1})^2+4\gamma_{e1}^{-1}\gamma_{e2}^{-1}\tilde{\Delta}_A^2}\right), \tag{36}$$

and above and below T_I they can be expressed as (for simplicity we put $\gamma_{e1}=\gamma_{e2}=\gamma_e$)

$$\gamma_e\tau_{e+}^{-1}=\begin{cases}\alpha_0(T-T_2)+36K(q_A-q_\theta)^2+\tilde{\Delta}_A(q=q_\theta), & T>T_I\\ 3\beta^2/8\gamma+4\alpha_0(T_I-T)+36Kq_A^2+\sqrt{(3\beta^2/8\gamma+4\alpha_0(T_I-T))^2+\tilde{\Delta}_A(q\geqslant q_\theta)^2}, & T<T_I,\end{cases} \tag{37}$$

$$\gamma_e\tau_{e-}^{-1}=\begin{cases}\alpha_0(T-T_2)+36K(q_A-q_\theta)^2-\tilde{\Delta}_A(q=q_\theta), & T>T_I\\ 3\beta^2/8\gamma+4\alpha_0(T_I-T)+36Kq_A^2-\sqrt{(3\beta^2/8\gamma+4\alpha_0(T_I-T))^2+\tilde{\Delta}_A(q\geqslant q_\theta)^2}, & T<T_I.\end{cases} \tag{38}$$

Above T_I (where A_0 is small and therefore $q\approx q_\theta$), the gap between e-mode phason and amplitudon frequencies increases to $2\tilde{\Delta}_A(q\approx q_\theta)=24K(q_A-q_\theta)q_\theta$, due to their coupling [compare Eqs. (35c), (35d) and (37), (38)], see Fig. 7. Below T_I, where $q_\theta<q<q_A$, there is an increase of the $1/\tau_{e+}$ frequency and decrease of $1/\tau_{e-}$ with respect to the noninteracting case. The most important feature is the temperature dependence of the BOO phason $1/\tau_{e-}$ near below T_I that hardens on cooling and finally saturates at lower temperatures (see Fig. 7). At the same time the temperature dependence of the BOO amplitudon $1/\tau_{e+}$ exhibits a smaller slope as compare with $1/\tau_{e1}$. The temperature dependence of the phason results from the nonzero value of $\tilde{\Delta}_A(q\geqslant q_\theta)$, and therefore q should be smaller than q_A in the hexatic phase. In Fig. 7, a schematic plot is shown keeping $q<q_A$ constant in the hexatic phase. Cooling below T_I the q can evolve increasing its value toward q_A, which causes the decrease of $\tilde{\Delta}_A$ and thus makes hardening of the modes even steeper.

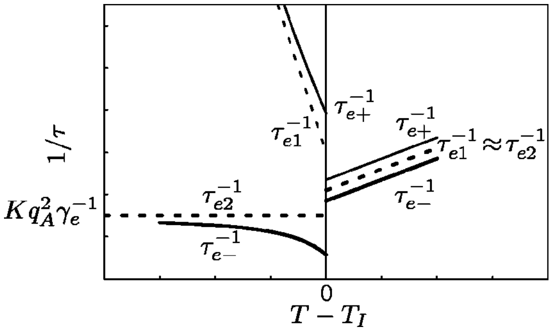

FIG. 7. Temperature dependence of the BOO relaxation frequencies (schematic plot). Dotted lines represent the case of noninteracting amplitudon and phason ($\tilde{\Delta}_A=0$). The interaction causes displacements of relaxation frequencies, increase of the gap and hardening of the phason below T_I (full lines).

Similar analysis can be done considering the coupling $\tilde{\Delta}_\theta$ of the tilt angle phason and amplitudon, the schematic plot is shown in Fig. 8. Above T_I when $q\approx q_\theta$ the phason and amplitudon do not interact since $\tilde{\Delta}_\theta\approx 0$. They are described by Eqs. (35a) and (35b). Below T_I, where $q>q_\theta$ and $\tilde{\Delta}_\theta(q)>0$, the gap between these modes increases with respect to Eqs. (35a) and (35b). It means that the magnitude of the increase of phason frequency in the hexatic phase (caused by the hexagonal potential) is partially reduced.

B. Susceptibility

The susceptibility is given by the equation

$$\chi(\omega)=\partial\langle P_x\rangle/\partial E_0=\langle P_x\rangle/E_0, \tag{39}$$

where $P_x=\frac{1}{2}(p+p^*)=-p_{10}\sin^2 qz-p_{20}\cos^2 qz$ is the polarization induced by the homogeneous electric field, and its spatial average across the sample dimension L reads

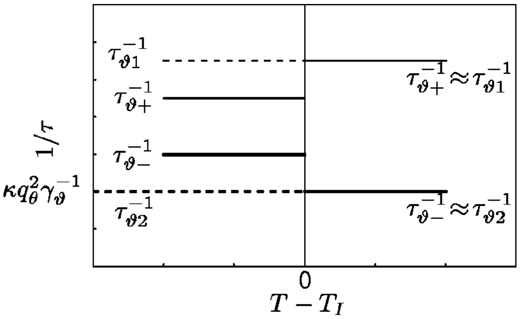

FIG. 8. Temperature dependence of the tilt relaxation frequencies (schematic plot). Dotted lines represent the case of the noninteracting amplitudon and phason ($\tilde{\Delta}_\theta=0$). The interaction that becomes nonzero below T_I causes displacements of relaxation frequencies, a decrease of the gap, but otherwise the relaxation frequencies remain temperature independent (full lines).

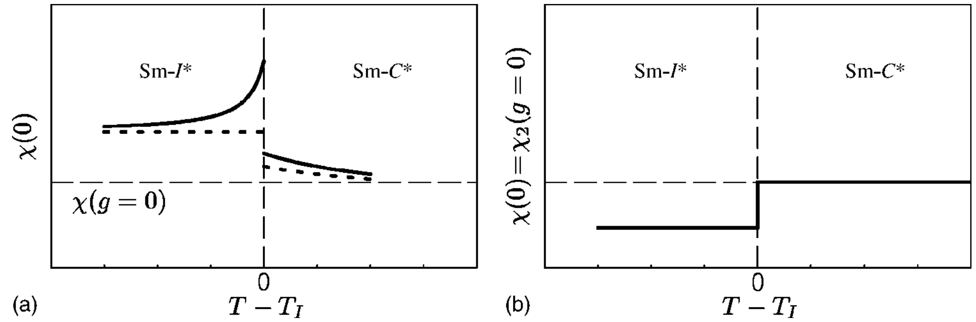

FIG. 9. Temperature dependence of the static susceptibility (schematic plot). (a) BOO contribution. The dotted line describes the noninteracting case when $\tilde{\Delta}_A=0$. The dashed horizontal line is a temperature independent background $\chi_2(g=0)$. The interaction between the BOO amplitudon and phason results in temperature dependent susceptibility in the hexatic phase. (b) Tilt angle contribution. The dashed horizontal line represents the case when the interaction between tilt and BOO is weak. In case of strong coupling of tilt and BOO, a susceptibility decrease in the hexatic phase is expected.

$$\langle P_x\rangle=\frac{1}{L}\int_0^L P_x \mathrm{d}z=-\frac{1}{2}(p_{10}+p_{20}). \tag{40}$$

The general expression for the susceptibility can be obtained solving Eqs. (33), (39), and (40)

$$\chi(\omega)=\tilde{\chi}_1+\tilde{\chi}_2, \tag{41}$$

$$\tilde{\chi}_2=-\frac{p_{20}}{E_0}=\chi_2\left(\frac{1-\chi_{12}\chi_1}{1-\chi_{12}^2\chi_1\chi_2}\right), \tag{42}$$

$$\tilde{\chi}_1=-\frac{p_{10}}{E_0}=\chi_1\left(\frac{1-\chi_{12}\chi_2}{1-\chi_{12}^2\chi_1\chi_2}\right), \tag{43}$$

$$\chi_2=\left(\chi_{p2}^{-1}-\frac{c^2\chi_{\vartheta 2}}{1-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi_{\vartheta 2}}-\frac{g^2\theta_0^{10}\chi_{e2}}{1-\tilde{\Delta}_A^2\chi_{e1}\chi_{e2}}\right)^{-1}, \tag{44}$$

$$\chi_1=\left(\chi_{p1}^{-1}-\frac{c^2\chi_{\vartheta 1}}{1-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi_{\vartheta 2}}-\frac{g^2\theta_0^{10}\chi_{e1}}{1-\tilde{\Delta}_A^2\chi_{e1}\chi_{e2}}\right)^{-1}, \tag{45}$$

$$\chi_{12}=\frac{c^2\tilde{\Delta}_\theta\chi_{\vartheta 1}\chi_{\vartheta 2}}{1-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi_{\vartheta 2}}+\frac{g^2\theta_0^{10}\tilde{\Delta}_A\chi_{e1}\chi_{e2}}{1-\tilde{\Delta}_A^2\chi_{e1}\chi_{e2}}. \tag{46}$$

When $\tilde{\Delta}_\theta=\tilde{\Delta}_A=0$ (and thus $q=q_\theta=q_A$) then there is no interaction between amplitudons and phasons and the susceptibility consists of the pure amplitudon contribution $\tilde{\chi}_1$ and the pure phason part $\tilde{\chi}_2$. Each of these terms can be expressed as a sum of two relaxators, BOO and tilt angle amplitudons and phasons, respectively, the eigenfrequencies of which are, up to terms proportional to $g^2\theta_0^{10}$, given by Eqs. (35a)–(35d). This case was discussed in Ref. [10], but without taking into account the elasticity of the BOO modulation (i.e., $\Lambda=K=0$ was considered). The presence of elasticity of BOO results in a shift of e-mode frequencies on Kq_A^2 in the hexatic phase.

When $q_\theta\neq q_A$, $\tilde{\Delta}_\theta$, $\tilde{\Delta}_A$ are nonzero, and the coupling between amplitudons and phasons exists. Consequently, $\tilde{\chi}_1$, $\tilde{\chi}_2$ yet cannot be treated as pure amplitudon and phason parts. We still assume, as usual, that the main contribution comes from the phasonlike part, $\chi(\omega)\approx\tilde{\chi}_2$. For simplicity we further assume that $(1-\chi_{12}\chi_1)/(1-\chi_{12}^2\chi_1\chi_2)\approx 1$. The contribution of the tilt phason $\chi_2(g=0)^{-1}=\chi_{p2}^{-1}-c^2\chi_{\vartheta 2}/(1-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi_{\vartheta 2})$ can be expressed as

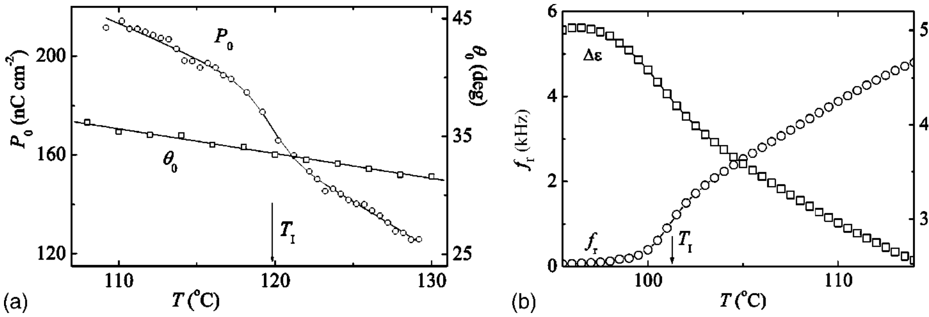

FIG. 10. Phase transition Sm-$C^*\rightarrow$Sm-I^* in (a) C8OCOOC6 [15] and (b) C8OCOOC5 [10]. (a) The tilt does not exhibit any anomaly at T_I (i.e., no competition between the tilt and BOO); polarization increases at T_I due to the increase of BOO according to Eq. (5). (b) The softening of the BOO phason and decrease of its frequency at T_I is in accord with $1/\tau_{e2}$ temperature behavior. The permittivity increases below T_I.

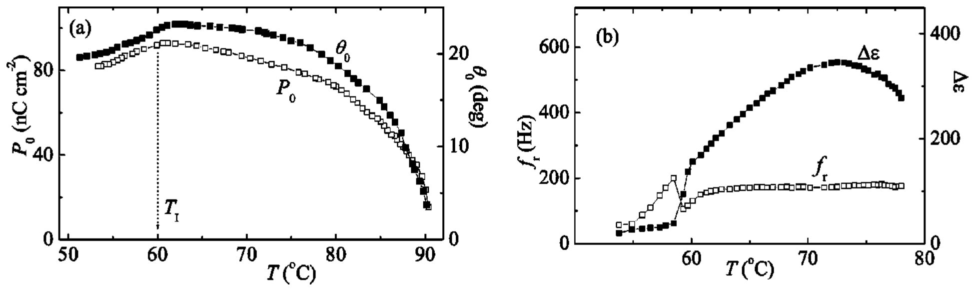

FIG. 11. Phase transition Sm-C^*→Sm-I^* in ZLL7/6 [16]. (a) Due to the appearance of BOO the tilt decreases on cooling in the hexatic phase (consequence of competition between the tilt and BOO). The same behavior shows polarization. (b) The relaxation frequency increases in the hexatic phase (similar to the behavior of $1/\tau_{\vartheta -}$). The permittivity decreases in the hexatic phase.

$$\chi_2(g=0)^{-1}=\chi(1-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi_{\vartheta 2})\times\left(1+\frac{(\tilde{\Delta}_\theta^2\chi_{\vartheta 1}+c^2)\chi\gamma_{\vartheta 2}^{-1}\tau_{\vartheta -}}{1+\mathrm{i}\omega\tau_{\vartheta -}}\right)\approx\chi\left(1+\frac{\chi c^2\gamma_{\vartheta 2}^{-1}\tau_{\vartheta 2}}{1+\mathrm{i}\omega\tau_{\vartheta 2}}\right), \qquad (47)$$

where $\tau_{\vartheta -}^{-1}=\tau_{\vartheta 2}^{-1}-\tilde{\Delta}_\theta^2\chi_{\vartheta 1}\chi\gamma_{\vartheta 2}^{-1}$, the last term being valid for $\tilde{\Delta}_\theta^2\approx 0$.

Then expanding with respect to $g^2\theta_0^{10}$ the phasonlike part of susceptibility can be written as

$$\chi(\omega)\approx\chi_2\approx\chi_2(g=0)\left(1+\frac{g^2\theta_0^{10}\chi_2(g=0)\gamma_{e2}^{-1}\tau_{e-}}{1+\mathrm{i}\omega\tau_{e-}}\right), \qquad (48)$$

where

$$\frac{\tau_{e+}}{\tau_{e1}}\frac{(1+\mathrm{i}\omega\tau_{e1})}{(1+\mathrm{i}\omega\tau_{e+})}\approx 1$$

is assumed and the relaxation frequencies $1/\tau_{e\pm}$ are given by Eqs. (37) and (38), and for $\tilde{\Delta}_A\approx 0$ they become $1/\tau_{e\pm}=1/\tau_{e1,e2}$. The relaxation frequencies of the e modes are assumed being lower than those of the tilt (it is reasonable in the vicinity of T_I and in the hexatic phase). Further we distinguish two cases that could explain dielectric spectra in the experiment.

1. Bond-order phason contribution

Let us neglect the local potential $10g|c|\chi\theta_0^4A_0$, which would cause a jump of $\chi_2(g=0)$ [see Eqs. (47) and (35b)]. This assumption means that the condensed hexatic order does not hinder rotation of the tilt. It could occur when, for instance, the amplitude A_0 of BOO remains relatively small in the hexatic phase. In the dispersion region of the BOO phason, the susceptibility of the tilt phason $\chi_2(g=0)$ is assumed frequency independent and the temperature dependence of the dielectric strength proportional to $g^2\theta_0^{10}$ is given by τ_{e2} or τ_{e-}, depending on whether the interaction between phason and amplitudon is important. The main feature here is an increase of the permittivity and a decrease of the relaxation frequency at the transition to the hexatic phase, see Figs. 9 and 8, respectively.

2. Tilt phason contribution

Here we consider the situation when the contribution of the BOO phason discussed above is negligible [i.e., $\chi(\omega)=\chi_2(g=0)$] and the frequency window of experiment cover the tilt angle phason dispersion. This situation can arise when the viscosity of the rotation of bond orientation, realized via diffusive motion of the whole molecules, is very high (i.e., $\gamma_{e2}^{-1}\rightarrow 0$). It is expected especially for highly developed hexatic order A_0. Then also the local potential in Eq. (35b) proportional to A_0 becomes important and the main contribution comes from the tilt angle phason $\chi_2(g=0)$. The static susceptibility proportional to $\tau_{\vartheta 2}$ exhibits a drop at the transition to the hexatic phase and the relaxation frequency $1/\tau_{\vartheta 2}$ increases.

Finally, let us mention the phase transition Sm-C^*→Sm-B_{hex}^* that is also described by the model. It is characterized by upright orientation of molecules in smectic layers in the hexatic phase, $\theta_0=0$, polarization is no longer coupled with BOO. The tilt angle phason in the Sm-B_{hex}^* phase disappears, and the mode of the tilt angle fluctuations (similar to the soft mode in the Sm-A phase) is the only dielectrically active one. This case is characterized by the disappearance of the observed relaxation process attributed to the phasons and the decrease of permittivity when entering the untilted hexatic phase from the Sm-C^* phase.

IV. SUMMARY AND COMPARISON WITH EXPERIMENTAL RESULTS

The theory describing static and dynamic properties in the vicinity of the phase transition to the hexatic phase is presented. Due to the competition between modulations of the molecular tilt and BOO, the incommensurate structure can appear in the finite temperature range around T_I, and in the hexatic phase the pitch of helix can change (increase or decrease) resulting in decrease of the molecular tilt angle. The temperature dependence of the tilt is in very good agreement with observations on several compounds, in which the tilt angle exhibits either no change or decrease, see Figs. 10 and 11. The phase diagram of the model also predicts so far not observed phase transition sequence Sm-C^*

$\rightarrow$Sm-I^*(Sm-F^*)$\rightarrow$Sm-B^*_{hex}, or a direct transition from the Sm-C^* phase to the untilted chiral hexatic Sm-B^*_{hex} phase due to the discontinuous character of the hexatic order appearance. However, the phase sequences Sm-$C\rightarrow$Sm-$F\rightarrow$Sm-B_{hex} and Sm-$C\rightarrow$Sm-B_{hex} were observed in nonchiral compounds [17,18]. To explain such sequences, the existence of an additional mechanism should be considered.

Dynamics is contributed by three amplitudons and three phasons of the fast polarization modes and slower tilt angle and BOO modes. The main contribution to the dielectric response is proposed to come from the tilt angle phason and (or) the BOO phason. When the BOO phason is strong enough, the softening of the relaxation frequency in the Sm-C^* phase occurs when approaching T_I, and the permittivity increases and the relaxation frequency decreases in the hexatic phase. In case when the tilt angle phason is the strongest mode, the softening of the relaxation frequency is not expected. Then instead increase of the relaxation frequency and decrease of permittivity should occur at T_I. Both these situations are suggested being observed in experiment, the first one in the substances C8OCOOC6 and C8OCOOC5 [10,15], and the latter one in compound ZLL7/6 [16].

In the experiment single relaxation was observed and fitted with the cole-cole expression with the exponent $\alpha<1$ (typically ~ 0.8), and the existence of two close processes could not be excluded. However, more probably the relaxation due to the tilt angle phason only can be expected, since the bond orientation variation connected with diffusive motion of the whole molecules is very slow, and the relaxation frequency of the BOO phason should occur in the frequency range, where it is overwhelmed by the low-frequency conductivity.

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[12] Both helices should reflect chirality of basic building blocks—chiral molecules.

[13] For $q>0$ and $q_A>q_\theta$, the proper signs in Eqs. (12a) and (12b) are "$-$" and "$+$," respectively.

[14] This is true when BOO rotation is substancially slower than the molecular rotation as assumed here.

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