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Tilt order parameters, polarity, and inversion phenomena in smectic liquid crystals

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The order parameters for the phenomenological description of the smectic-*A* to smectic-*C* phase transition are formulated on the basis of molecular symmetry and structure. It is shown that, unless the long molecular axis is an axis of twofold or higher rotational symmetry, the ordering of the molecules in the smectic-*C* phase gives rise to more than one tilt order parameter and to one or more polar order parameters. The latter describe the indigenous polarity of the smectic-*C* phase, which is not related to molecular chirality but underlies the appearance of spontaneous polarization in chiral smectics. A phenomenological theory of the phase transition is formulated by means of a Landau expansion in two tilt order parameters (primary and secondary) and an indigenous polarity order parameter. The coupling among these order parameters determines the possibility of sign inversions in the temperature dependence of the spontaneous polarization and of the helical pitch observed experimentally for some chiral smectic-C^* materials. The molecular interpretation of the inversion phenomena is examined in the light of this formulation.

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I. INTRODUCTION

The molecular physics of smectic liquid crystals has been receiving much attention, mainly in connection with ferroelectricity-related applications of some of these materials [1]. Nearly three decades ago it was predicted by Meyer, and soon afterward proved experimentally, that a tilted smectic-*C* phase made of chiral molecules can exhibit spontaneous electric polarization P_S within each smectic layer [2]. This chiral phase, the Sm-C^*, further differs from the achiral (Sm-*C*, handedness symmetric) phase in that the azimuthal angle of the director varies linearly with the distance along the layer normal, thus defining a helical configuration of definite handedness and constant pitch. Normally, P_S disappears on heating to the nontilted (orthogonal) smectic-*A* (Sm-*A*) phase. More recently, spontaneous polarization was detected in a special class of achiral compounds with bent structure (banana-shaped molecules) forming smectic phases with form chirality [3–5].

In general, P_S depends very sensitively on the structure of the molecules that form the Sm-C^* phase. There are numerous examples of dramatic changes in P_S caused by only slight modifications of the molecular structure. Usually, the magnitude of P_S increases on lowering the temperature from the Sm-*A*–Sm-C^* transition point $T_{A\text{-}C^*}$. A number of Sm-C^* compounds, however, deviate from this behavior in that the magnitude of P_S increases up to some value from which it decreases on further reducing the temperature. In several known cases the decrease of $|P_S|$ with temperature continues until an "inversion temperature" T_{inv} is reached at which P_S vanishes completely; below that temperature P_S grows again monotonically but with the opposite sign [6–11]. The temperature dependence of the tilt angle and of the helical pitch does not show any particular irregularity around the inversion temperature of P_S. Certain compounds exhibit inversion of the pitch handedness [12] with temperature but this does not seem to be directly correlated with the sign inversion of P_S. In one known case where both types of inversion are exhibited by the same compound, the two inversions happen at different temperatures [13]. A sign-inverting behavior of P_S with temperature has also been observed in side-chain Sm-C^* polymers [14]. A similar sign inversion is observed, as a function of concentration, in mixtures of achiral smectic molecules with chiral dopants [15].

One interpretation proposed for the sign inversion of P_S with temperature is based on the mechanism of competing conformations that produce opposite contributions to the spontaneous polarization [7,13]. Another interpretation assumes competing effects originating from the polar and quadrupolar biasing of rotations around the long molecular axis and attributes the sign reversal to a special case of the coupling of the tilt to the rotational biasing [16]. Although these two interpretations address different molecular features, namely, conformational changes and transverse interactions, they are not necessarily mutually exclusive. In fact, the possibility of sign reversal of P_S is directly obtained in a molecular theory of primitive smectic molecules consisting of a rigid mesogenic core and two pendant chains that can rotate about the core axis, thus producing different conformations [17,18]. This theory explicitly shows that the tilt angle of the core segments is in general different from the tilt of the chains and that the sign inversion of P_S is related to the variation of this difference. The variation is driven by packing correlations between the molecular orientations and the conformations. Such correlations affect both the conformational sampling and the sampling of transverse intermolecular interactions that produce the rotational bias of a given conformer around the long molecular axis.

Notably, each of the above interpretations implies molecular features, such as biaxiality and flexibility, that are clearly beyond the uniaxial rod idealizations underlying the simplest microscopic and phenomenological descriptions of

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tilted smectics. The consideration of more realistic molecular structures is necessary not only for the interpretation of special phenomena, such as the inversion of the spontaneous polarization or of the pitch, but also for the understanding of more common and fundamental aspects of smectics, such as microsegregation. The latter originates from the chemical differentiation of the two basic components of the smectic molecules, namely, the relatively rigid mesogenic core and the aliphatic end chains. Microsegregation is the mechanism that drives the formation of the smectic layers and, combined with the nonlinear (zigzag, bent, etc.) structure of the molecules, gives rise to tilt and polar ordering [17,18]. In common smectic molecules, molecular flexibility consists mainly of internal flexibility of the end chains and of the possibility of rotations of the chains as a whole relative to the core. In the absence of any site-specific interactions, flexibility alone could produce microsegregation as it is entropically favorable for the ''fluid'' chains to group together [19]. Furthermore, as a result of the internal relative motions of the submolecular segments, the average disposition of the flexible, asymmetric, molecule in the tilted smectic phase cannot in general be described by a single tilt angle (equivalently, by a single ''director''). Different segments of the molecule could exhibit different tilt angles with respect to the layer normal.

The existence of more than one director, and associated tilt angle, has been invoked for the interpretation of the results of several experimental studies of the Sm-*C* phase. Deuterium NMR measurements [20] indicate that different segments of the flexible smectic molecules do not in general share a common principal axis (director) of their second rank ordering tensors. A clear difference between the tilt angles associated with the mesogenic core and the flexible end chains of the molecules is obtained from x-ray measurements [21] in the Sm-*C* phase. Analogous conclusions are reached with IR spectroscopy [22]. It is also well known that x-ray measurements and optical measurements give in general different values for the tilt angle, indicating that the tilt determined from molecular packing within the layers need not coincide with the deviation of the principal optical axis from the layer normal. Such considerations are consistent with recent results from combined x-ray and optical studies on ferroelectric liquid crystal cells [23]. In fact, a single tilt angle description is strictly applicable only to molecules of uniaxial symmetry.

The same implications of molecular asymmetry and flexibility are carried over to the polar order parameters; they are in general different for different segments of the molecule. This is directly demonstrated by atomistic calculations of the segmental order parameters [24]. It is also in accord with the observed sensitivity of the spontaneous polarization of some categories of Sm-C^* compounds to changes of the position of the electric dipole moment within the molecular frame [1,24].

This paper is concerned with the incorporation of molecular symmetry and flexibility in the phenomenological description of the Sm-*A*–Sm-*C* phase transition. The resulting formulation is used to analyze the sign inversion of the spontaneous polarization and of the pitch observed in some Sm-C^* materials since such phenomena are thought to reflect particular effects of molecular structure and conformation on smectic ordering.

The next section deals with the identification of the relevant order parameters of the Sm-*A* and Sm-*C* phases in relation to molecular structure and symmetry. These order parameters are then used in Sec. III to formulate a Landau expansion of the free energy of the Sm-*A*–Sm-*C* transition. The Landau expansion is used to derive the temperature dependence of the order parameters and therefrom to investigate the conditions leading to sign inversion of the parameters associated with the spontaneous polarization, in Sec. IV, and the handedness of the pitch in the Sm-C^* phase, in Sec. V. The current description is compared with the conventional Landau expansion in Sec. VI.

II. SYMMETRIES AND ORDER PARAMETERS

The Sm-*C* phase has a mirror symmetry plane, the ''tilt plane,'' perpendicular to the layers, and a twofold rotation symmetry axis (C_2) in the direction normal to the tilt plane [1,2]. The intersection of the twofold axis with the mirror plane defines the center of inversion symmetry of the phase. In what follows, the layer normal is identified as the *Z* axis of a phase-fixed reference frame and the twofold symmetry axis is taken to be the *X* axis of the frame. Accordingly, the above symmetries imply invariance of the molecular probability distribution, and thereby of the free energy of the phase, with respect to the following two transformations:

$$X \to -X \quad (\text{plane of symmetry}), \tag{1}$$

$$(Y,Z) \to (-Y,-Z) \quad (\text{twofold rotation}). \tag{2}$$

As a result of the invariance with respect to these transformations, the phase is also invariant with respect to change of handedness of the *XYZ* frame, i.e., achiral. The symmetry of the Sm-*A* phase differs in that it is invariant separately with respect to

$$Y \to -Y \quad \text{and} \quad Z \to -Z. \tag{3}$$

A. Uniaxial molecules

If the molecules forming the smectic phase are approximated by uniaxially symmetric rigid objects, then the orientation of each molecule is specified in terms of a single unit vector **s** along the molecular axis of full rotational symmetry [see Fig. 1(a)]. In that case, the orientational order parameters, i.e., the ensemble averages of tensors of various ranks that can be formed from the components of **s**, reflect the symmetries of the Sm-*C* phase in the following ways. The zero rank (scalar) order parameters are trivial ($\langle \mathbf{s}^2 \rangle = 1$) in view of the assumed rigidity of the molecules. The first rank (vector) order parameters vanish in view of Eqs. (1) and (2),

$$\langle s_X \rangle, \langle s_Y \rangle, \langle s_Z \rangle = 0. \tag{4}$$

The second rank order parameters are the components of the symmetric and traceless tensor

$$\eta_{ab} = (3\langle s_a s_b \rangle - \delta_{ab})/2, \tag{5}$$

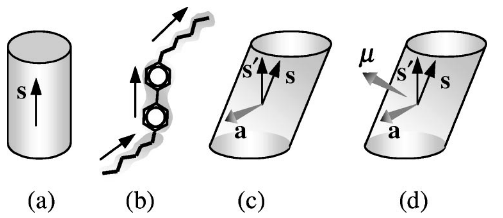

FIG. 1. (a) Right cylinder representing the molecular symmetry of rigid uniaxial molecules. The unit vector **s** defines the direction of the axis of full rotational symmetry of the molecule. (b) Coarse representation of the generic structure of real smectic molecules in the most symmetric case. The molecules have a plane of (statistical) symmetry (mirror plane, coinciding with the plane of the drawing), an axis of twofold rotational symmetry (perpendicular to the symmetry plane), and an inversion center (at the point where the twofold axis intersects the mirror plane). The three arrows represent the vectors describing the direction of the mesogenic core and of the axes of the two end chains in their most extended conformation. (c) Oblique cylinder representation of a molecule bearing the same symmetries as in (b) but disregarding other structural and conformational features. The two unit vectors **s** and **s**′ are rigidly attached to the molecule; they specify its orientation and define its mirror symmetry plane. The pseudovector $\mathbf{a}=\mathbf{s}\times\mathbf{s}'$ is normal to the symmetry plane. (d) A dipole moment $\boldsymbol{\mu}$ is attached to the oblique cylinder in (c). If $\boldsymbol{\mu}$ has a nonvanishing component in the direction of **a**, the attachment of the dipole leads to the breaking of the mirror symmetry. The molecule then becomes chiral with respect to its electrostatic interactions.

with the subscripts a,b denoting components along the X,Y,Z axes. The order parameters η_{XY} and η_{XZ} vanish as a result of the symmetry transformation in Eq. (1). The diagonal components $\eta_{XX},\eta_{YY},\eta_{ZZ}$ survive both symmetry operations in Eqs. (1) and (2) and so does the off diagonal component η_{YZ}. The latter gives a measure of the breaking of the rotational symmetry about the layer normal (Z axis) due to the tilted ordering of the molecules. The additional symmetry, Eq. (3), of the Sm-*A* phase leads to $\eta_{YZ}=0$. Thus the primary order parameter for the distinction between the Sm-*A* and the Sm-*C* phases is η_{YZ}.

It is convenient not to use directly the order parameter η_{YZ} in the phenomenological description of the phase transition but rather to use the so-called "tilt pseudovector" **t**, which conveys explicitly the deviation of the director from the layer normal in the Sm-*C* phase. The relation of **t** to η_{YZ} is established through the identification of the director with the principal axis of the ordering tensor. The tilt pseudovector is defined by

$$\mathbf{t}=(\mathbf{Z}\times\tilde{\mathbf{Z}})(\mathbf{Z}\cdot\tilde{\mathbf{Z}}), \tag{6}$$

where $\tilde{\mathbf{Z}}$ is the unit vector in the direction of the principal axis of the ordering tensor η_{ab}. The principal axis frame $\tilde{X}\tilde{Y}\tilde{Z}$ is obtained by rotating the XYZ frame about the X axis by an angle θ such as to diagonalize the tensor η_{ab}, i.e., to obtain the frame for which $\eta_{\tilde{Y}\tilde{Z}}=0$ or, equivalently, for which the order parameter η_{ZZ} acquires its maximum value $\eta_{\tilde{Z}\tilde{Z}}$. Obviously $\tilde{X}$ coincides with X and the pseudovector **t** is along X. The angle θ is related to the tilt pseudovector and to the components of η_{ab} as follows:

$$\sin 2\theta=2\mathbf{X}\cdot\mathbf{t}=2\,\eta_{YZ}/(\eta_{\tilde{Z}\tilde{Z}}-\eta_{\tilde{Y}\tilde{Y}}). \tag{7}$$

Since the onset of the (achiral) Sm-*C* phase is marked simply by the appearance of a non-vanishing value of the tilt vector, the Landau expansion [1] of the equilibrium free energy difference $g_{A\text{-}C}$ describing the Sm-*A*–Sm-*C* phase transition is an expansion in the single order parameter **t**. Furthermore, due to the thermodynamic equivalence of the states with **t** and −**t**, the expansion contains only even powers of **t**,

$$g_{A\text{-}C}=\frac{1}{2}at^2+\frac{1}{4}bt^4+\cdots. \tag{8}$$

This is the conventional form of the Landau expansion for the Sm-*A*–Sm-*C* transition in the absence of external fields [25–28]. It clearly does not involve any kind of polarity order parameter. It should be recalled, however, that this description is valid only under the assumption that a single vector **s** is sufficient to describe the molecular orientation, or, equivalently, that the molecules in the smectic phase behave as rigid uniaxial objects. It is, of course, not implied here that perfectly uniaxial molecules can indeed form a Sm-*C* phase.

The phenomenological description obtained in this section, i.e., the expression for the tilt pseudovector in Eq. (6), also known as the Pikin-Indenbom order parameter [1], and the conventional form of the Landau expansion in Eq. (8), could be obtained without any reference to molecular structure or symmetry. This could be done simply by assuming that the orientational ordering of the molecules can be fully described by a single order parameter tensor of rank 2. This idealization leads to a single director $\tilde{\mathbf{Z}}$ which, when not coincident with the layer normal **Z**, can be used to define the tilt order parameter according to Eq. (6). Molecular structure and symmetry have been explicitly considered in this section in order to facilitate the subsequent discussion of less idealized representations of molecular organization in tilted smectics.

B. Minimal deviation from uniaxial molecules

Real smectic molecules are of course flexible, their shape is not uniaxial, and their orientation within the smectic phase cannot be fully specified by a single vector [see Fig. 1(b)]. In fact the complete specification of the orientation and conformation of the molecule requires at least as many unit vectors as there are molecular segments capable of moving relative to one another. In what follows we demonstrate that the description of the Sm-*A*–Sm-*C* phase transition becomes qualitatively different if one goes beyond the uniaxial idealization of the molecular structure. This will be done by minimally extending the single vector description to a description in terms of two molecular unit vectors but the formulation can be readily generalized to more complex molecular structures.

Consider a molecular structure such as the one shown in Fig. 1(b). In the most symmetrical case the structure is centrosymmetric, the plane of the fully extended conformation of the molecule is a mirror symmetry plane, and the axis perpendicular to that plane at the inversion center of the molecule is a twofold symmetry axis. Ignoring for the moment molecular flexibility and structural details, these symmetries are conveyed by the oblique cylinder of Fig. 1(c). Unlike the right cylinder of Fig. 1(a), the orientation of this object cannot be completely specified by a single unit vector **s**. A second unit vector **s**′ is required. A convenient choice of unit vectors **s**, **s**′ is shown in Fig. 1(c). A measure of the deviation from prefect rotational symmetry about a single ''long'' axis is then provided by the pseudovector $\mathbf{a}=\mathbf{s}\times\mathbf{s}'$. This pseudovector is normal to the symmetry plane of the oblique cylinder; its direction can be used to differentiate between the two ''faces'' of the molecule, i.e., the two halves of the molecule separated by the symmetry plane. Obviously, these two halves of the oblique cylinder are distinct mirror images of each other; equivalently, the two ''faces'' of the molecule are distinguishable.

The symmetries of Eqs. (1) and (2) imply that the first rank order parameters associated with the two unit vectors of the oblique cylinder vanish, $\langle\mathbf{s}\rangle=0=\langle\mathbf{s}'\rangle$. By analogy with Eq. (5) there are two second rank order parameter tensors, one for each of the vectors **s**,**s**′, namely,

$$\eta_{ab}^{(s)}=(3\langle s_a s_b\rangle-\delta_{ab})/2, \tag{9}$$

and

$$\eta_{ab}^{(s')}=(3\langle s'_a s'_b\rangle-\delta_{ab})/2. \tag{10}$$

There is also a third, mixed, second rank order parameter tensor

$$\eta_{ab}^{(s,s')}=(3\langle s_a s'_b+s'_a s_b\rangle/2-(\mathbf{s}\cdot\mathbf{s}')\,\delta_{ab})/2. \tag{11}$$

Only the YZ off diagonal components of these tensors survive the symmetry operations in Eqs. (1) and (2). Now, the diagonalization of each of the tensors $\eta_{ab}^{(s)}$, $\eta_{ab}^{(s')}$, and $\eta_{ab}^{(s,s')}$ requires in general a different rotation about the X axis. Accordingly, there are three different tilt angles $\theta^{(s)},\theta^{(s')}$, and $\theta^{(s,s')}$ defining three different director frames (frames of principal axes). The three tilt angles, and the associated tilt vectors $\mathbf{t}^{(s)},\mathbf{t}^{(s')}$, and $\mathbf{t}^{(s,s')}$, are related to the components of the respective tensors analogously to Eqs. (6) and (7). As shown in Appendix A, the choice of the three independent tilt order parameters to represent the breaking of the rotational symmetry about the layer normal is not unique. It is also shown there that, in the case of perfectly rigid molecules, one of the three parameters can be eliminated by choosing the molecular frame of axes properly.

The existence of more than one tilt order parameter is not the only difference from the uniaxially symmetric molecules. Another, perhaps more important, difference is that the pseudovector **a** singles out a unique transverse molecular direction and this makes it possible to define the (pseudovector) order parameter $\langle\mathbf{a}\rangle$. The Y and Z components of $\langle\mathbf{a}\rangle$ vanish as a result of the symmetry operations of Eqs. (1) and (2), but the X component survives these operations and therefore the corresponding order parameter

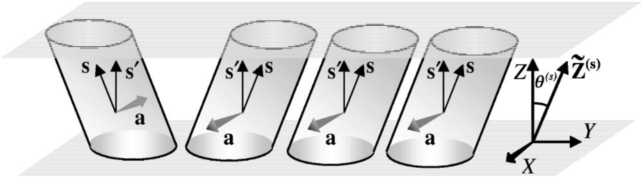

FIG. 2. Illustration of the packing mechanism giving rise to polar ordering within a single layer of the tilted phase. With the director $\tilde{\mathbf{Z}}^{(s)}$ tilted to the right relative to the layer normal, the statistically dominant molecular configurations are represented by the three oblique cylinder molecules on the right. For such configurations, the pseudovector **a** points out of the plane of the figure (the ''tilt plane''). Molecules configured like the oblique cylinder on the left end have **a** pointing into the plane of the figure but these configurations deviate from the preferred tilt direction and are therefore statistically less favored by the packing constraints. Accordingly, the average projection of the pseudovector **a** along the direction normal to the plane of the figure (the C_2 axis of the phase) will not vanish. The value of this projection defines the indigenous polarity order parameter $\mathbf{P}_I$ of Eq. (13). The molecules chosen for this illustration have a plane of mirror symmetry (perpendicular to **a**) in order to stress that the polarity of the tilted phase has nothing to do with molecular chirality.

$$\langle a_X\rangle=\langle s_Y s'_Z-s'_Y s_Z\rangle \tag{12}$$

acquires a nonvanishing value in the Sm-*C* phase. This order parameter describes the indigenous polar ordering [17] exhibited by the molecules as a result of the tilted alignment within the smectic layers. The microscopic origin of the indigenous polarity is depicted in Fig. 2 for the molecules whose shape can be approximated by the oblique cylinders of Fig. 1(c): with the director $\tilde{\mathbf{Z}}^{(s)}$ tilted to the right of the Z axis and with the X axis pointing outward from the plane of the figure, the combination of stratification and alignment constraints favors the molecular configurations for which **a** points in the positive direction of the X axis $(\mathbf{a}\cdot\mathbf{X}>0)$ over those for which **a** points in the negative direction $(\mathbf{a}\cdot\mathbf{X}<0)$. Accordingly, on the average $\mathbf{a}\cdot\mathbf{X}$ will acquire a positive value $\langle a_X\rangle$.

The existence of the tilt-induced polar ordering was demonstrated using explicit molecular models of the Sm-*C* phase taking into account phase symmetry and orientation-conformation correlations dictated by the tilted stratified ordering [17,18]. It was also pointed out that this type of polar ordering, the indigenous polarity, was overlooked in all previous molecular theories of tilted smectics. For notational convenience, the polar ordering can be represented by an indigenous polarity (pseudovector) order parameter $\mathbf{P}_I$ directed along the X axis of the phase and defined as follows:

$$\mathbf{P}_I=\langle\mathbf{a}\rangle/|\mathbf{a}|=\mathbf{X}\langle a_X\rangle/|\mathbf{a}|. \tag{13}$$

C. Spontaneous polarization and molecular chirality

Clearly, the indigenous polarity is not a result of molecular chirality and is present irrespective of whether or not the phase exhibits an electric spontaneous polarization $\mathbf{P}_S$. In fact, the appearance of spontaneous polarization can be considered as a manifestation of the indigenous polarity when the smectic molecules possess a permanent dipole moment. For example, if the oblique cylindrical molecules in Fig. 2 possess a dipole moment $\boldsymbol{\mu}$, rigidly attached to the molecular frame [see Fig. 1(d)] and with a nonvanishing component along $\mathbf{a}$, then the indigenous polarity gives rise to a spontaneous polarization vector $\mathbf{P}_S$ along the X axis. As shown in Appendix B, the spontaneous polarization $\mathbf{P}_S$ can in this case be expressed in terms of the indigenous polarity order parameter $\mathbf{P}_I$ according to :

$$\mathbf{P}_S = \mathcal{N}\mu_\perp^* \mathbf{P}_I, \tag{14}$$

where $\mathcal{N}$ is the number of molecules per unit volume and $\mu_\perp^* \equiv (\boldsymbol{\mu}\cdot\mathbf{a})/|\mathbf{a}|$ is the (pseudoscalar) measure of what is often referred to as the ''transverse molecular dipole.'' Equation (14) is an exact result relating a macroscopic quantity ($\mathbf{P}_S$) to a molecular order parameter ($\mathbf{P}_I$) via a molecular property ($\mu_\perp^*$). It states that the (indigenous) polar ordering of the Sm-*C* phase will give rise to a macroscopic polarization provided that $\mu_\perp^* \neq 0$. It should be noted at this point that the presence of a dipole moment with a nonvanishing component along $\mathbf{a}$ breaks the mirror symmetry of the oblique cylindrical molecule, i.e., introduces a chiral asymmetry. It is clear, however, that this chiral asymmetry does not produce the polar ordering; it is involved only with the manifestation of the latter in the form of an electric spontaneous polarization.

It is perhaps instructive to view Eq. (14) as an explicit realization of the general relation proposed by de Gennes and Prost [29] on purely dimensional grounds:

$$\begin{aligned}&(\text{spontaneous polarization})\\ &\quad=(\text{number of molecules per unit volume})\\ &\qquad\times(\text{transverse molecular dipole})\\ &\qquad\times(\text{yield factor}). \end{aligned}\tag{15}$$

Since the spontaneous polarization is a true vector and since the physical quantity ''transverse molecular dipole'' has to change sign on transforming the molecule to its mirror image, there are in principle two possibilities for the tensor character of the ''transverse molecular dipole'': either vector or pseudoscalar. In the first case the order parameter that goes under the name of ''yield factor'' must be a scalar and in the second a pseudovector. Obviously Eq. (14) corresponds to the second possibility and the ''yield factor'' is identified with the indigenous polarity pseudovector $\mathbf{P}_I$. Although both possibilities are acceptable from the tensorial point of view, the first possibility is physically incorrect since the direction of the spontaneous polarization vector is a macroscopic one and cannot therefore be specified by any directional quantity associated with individual molecules but rather by the directionality of an order parameter describing the bulk phase, in this case the ''yield factor'' $\mathbf{P}_I$.

For conceptual clarity we have used an idealized molecular picture where the introduction of a dipole moment in the molecular structure has negligible effects on the molecular shape and on the intermolecular interactions. This is approximately true for some types of real compounds. Normally, the chemical introduction of lateral dipolar groups deforms to some extent the molecular structure to a shape without mirror plane symmetry. Furthermore, if the dipole moments are strong enough the effects of dipole-dipole interactions on the molecular ordering, and in particular on $\mathbf{P}_I$, could become appreciable. Here, however, our primary interest is not in these effects but rather in the polar order that persists in the limit of perfect mirror symmetry of the molecular shape and of vanishing dipole-dipole interactions, for which the idealized molecular picture is appropriate. Accordingly, the introduction of dipole moments to the molecular structure is assumed to break only the mirror plane symmetry of the electrostatic profile of the molecule (not its shape, i.e., its packing properties in the bulk). A measure of this ''electrostatic chirality'' for the idealized structure of Fig. 1(d) is given by $\mu_\perp^*$. This measure of molecular chirality is, of course, not a universal one. Its relevance is restricted to the description of the spontaneous polarization. Other manifestations of chirality, such as the helical twisting power, involve different quantifications of molecular chiral asymmetry [30].

The example of the oblique cylinder was used here as a minimal deviation from rotationally symmetric molecular structures to provide a simple concrete illustration of the mechanisms underlying the relation of polarity to tilted ordering. However, the basic conclusions reached in this section, namely, that the molecular ordering in the Sm-*C* phase is intrinsically polar and not adequately described by just a single tilt order parameter (or a single ''director''), can be readily carried over to more realistic examples of molecular structure and flexibility.

III. LANDAU EXPANSION

Given that there is more than one tilt order parameter and at least one indigenous polarity order parameter, it is necessary to describe how these order parameters are incorporated in the phenomenological Landau expansion of the free energy for the Sm-*A*–Sm-*C* phase transition. This is addressed in the present section using, for simplicity, the example of molecules with the symmetries of the oblique cylinder.

Since there are three second rank tensors, as in Eqs. (9)–(11), the diagonalization of which defines three different tilt vectors, the formulation of a Landau expansion is not as straightforward as in the case of a single tilt vector. Obviously, any linear combination of the three tensors constitutes a new tensor whose diagonalization defines a tilt vector. It is thus possible to use in place of the original three tensors any three linearly independent combinations thereof (see Appendix A). Of course all such choices are physically equivalent and the corresponding expansions can be transformed into one another. The actual choice is therefore dictated by considerations of simplicity and physical clarity. As shown in Appendix A, a description in terms of just two independent tilt vectors can be obtained in the case of rigid molecules by properly choosing the molecular frame. The explicit consideration of several molecular segments and tilt vectors without restrictions on flexibility, is treated in detail elsewhere [31]. Here we consider systems that can be described in terms of two tilt vectors $\mathbf{t}$ and $\mathbf{t}'$, both of which acquire nonzero values at the same transition temperature T_{A-C}. The tilt vectors $\mathbf{t}$ and $\mathbf{t}'$ will be referred to as the primary and secondary tilts, respectively. Physically, the primary tilt could be assigned to represent, for example, the tilted ordering of the mesogenic core and the secondary tilt to represent the effective mean tilt of the pendant chains. Another possibility for the physical content of $\mathbf{t}$ and $\mathbf{t}'$ is to describe the average tilt of the overall molecule $(\mathbf{t})$ and the weighted spread in the tilts exhibited by the different molecular segments $(\mathbf{t}')$. Similarly, a single polarity parameter $\mathbf{P}_I$ will be used, which is understood to represent the polar ordering of a unit pseudovector defined by the vector product of two appropriately chosen molecular vectors.

With all three pseudovectors $\mathbf{t},\mathbf{t}',\mathbf{P}_I$ along the $X(C_2)$ axis, the rotational invariants that can enter into the extended Landau expansion are the scalar quantities $(\mathbf{t}\cdot\mathbf{t}),(\mathbf{t}'\cdot\mathbf{t}')$, $(\mathbf{P}_I\cdot\mathbf{P}_I),(\mathbf{t}\cdot\mathbf{t}'),(\mathbf{t}\cdot\mathbf{P}_I)$, and $(\mathbf{t}'\cdot\mathbf{P}_I)$. Accordingly, the extended version of the expansion of Eq. (8) for the free energy of a single smectic layer contains the following leading terms:

$$g_{A\text{-}C}=\frac{1}{2}\ at^2+\frac{1}{2}a't'^2-ctP_I-c't'P_I+c''tt'+\frac{1}{2}dP_I^2$$
$$+\frac{1}{4}bt^4+\cdots. \tag{16}$$

Here the pseudovectors $\mathbf{t},\mathbf{t}',\mathbf{P}_I$ are replaced, for notational simplicity, by their projections t,t',P_I along the X axis. The coefficients a,a',b,c,c',c'',d are all scalar (handedness symmetric) quantities. The coefficient d is associated with the decrease in entropy resulting from the polar ordering within the smectic layer and is therefore positive $(d>0)$. The signs of the coefficients c,c',c'', associated with the bilinear coupling contributions among the parameters t,t',P_I, depend on the choice of the relative signs of the molecular vectors. The differentiation between the primary tilt t and the secondary t' in the expansion is made by the inclusion of a fourth power contribution only for the former, with $b>0$, and by the strong temperature dependence of the coefficient a. The latter coefficient is assumed to change sign with temperature near the Sm-A–Sm-C transition, whereas the coefficient a' is assumed to be, like all the other coefficients, slowly varying with temperature around the transition. For flexible molecules, however, the variation of the conformational statistics (and thereby of the "effective" molecular structure) with temperature could considerably enhance the temperature dependence of these coefficients. The sign of a' is assumed to be positive, corresponding to the dominance of the entropy decrease associated with the secondary tilt over the respective lowering of the internal energy. Higher order terms have been omitted from the expansion in Eq. (16) to avoid excessive mathematical burden. However, terms such as $P_I^2t^2$ could be of particular importance for the correct description of the underlying physics and are therefore not negligible in general [1,27].

Minimization of the free energy in Eq. (16) with respect to t,t', and P_I yields the following expressions for these order parameters in terms of the expansion coefficients:

$$t^2=(h-a)/b, \tag{17}$$

$$t'/t=r, \tag{18}$$

$$P_I/t=R, \tag{19}$$

where

$$h\equiv[c^2+(cc'-c''d)^2/(a'd-c'^2)]/d, \tag{20}$$

$$r\equiv(cc'-c''d)/(a'd-c'^2), \tag{21}$$

and

$$R\equiv(a'c-c'c'')/(a'd-c'^2). \tag{22}$$

It is usually assumed that the strong dependence of a on temperature near the phase transition is adequately described by the form

$$a/b\approx a_1(T-T_0), \tag{23}$$

with a_1 constant and positive and T_0 a characteristic temperature constant. For T near $T_0,h/b$ can be approximated by

$$h/b\approx h_0+h_1(T-T_0), \tag{24}$$

with h_0,h_1 constants. Normally $|h_1|\ll a_1$, reflecting the weak dependence of h/b on temperature. It then follows from Eqs. (17), (23), and (24) that near the Sm-A–Sm-C phase transition the temperature dependence of the primary tilt is of the form

$$t^2\approx t_0^2(T_{A\text{-}C}-T), \tag{25}$$

where the phase transition temperature $T_{A\text{-}C}$ is given by

$$T_{A\text{-}C}=T_0+h_0/(a_1-h_1), \tag{26}$$

and the constant scale factor in Eq. (25) is $t_0^2=a_1-h_1$.

IV. SIGN INVERSION OF THE POLARITY ORDER PARAMETER

Consider next the coefficient R of Eq. (22). If the temperature dependence of all the coefficients entering the expression for R were neglected then, according to Eq. (19), the ratio P_I/t would be constant with temperature and it would follow from Eq. (25) that $P_I\sim\sqrt{T_{A\text{-}C}-T}$. However, it is apparent from Eq. (22) that this is not necessarily the case. Although each of the coefficients is taken individually to vary slowly with temperature, their combination could exhibit a rapid variation. Specifically, the combination $c'c''/a'$ represents the couplings of the primary tilt and of the polarity to the secondary tilt, scaled by the coefficient of the entropic contributions of the latter. If this quantity is nearly equal to the coupling c of the polarity to the primary tilt then the numerator on the right hand side of Eq. (22) will be very sensitive to the temperature dependence of these two, mutually canceling, terms. The effect could be further magnified by reduction of the magnitude of the denominator if c'^2, associated with the coupling of polarity to the secondary tilt, is not small compared to the product $a'd$ associated with the entropic contribution of these two parameters. Stated more briefly, R is sensitive to the relative strength of the coupling of the polarity to the primary and secondary tilts. Two extreme situations can be considered, corresponding to the complete decoupling of the polarity from one of the tilt parameters. Thus if P_I is completely decoupled from t', i.e., if $c'=0$, then from Eq. (22) $R=c/d$. In the other extreme, polarity is exclusively coupled to the secondary tilt, i.e., $c=0$, and then $R=-c'c''/(a'd-c'^2)$. In either of the decoupled cases, the temperature dependence of R does not involve mutually canceling terms and is weaker than in the fully coupled case.

To relate these considerations to the possible temperature dependence of P_I we note that, quite generally, the temperature dependence of R may be approximated near the transition temperature by

$$R\approx R_0+R_1(T-T_{A\text{-}C}), \tag{27}$$

where R_0, R_1 are constants. Now, for the cases where, as described above, R_1 is not negligible relative to R_0, it is useful to define a characteristic polarity-inversion temperature by

$$T^P_{inv}\equiv T_{A\text{-}C}-R_0/R_1. \tag{28}$$

Near the transition temperature, R can be expressed in terms of T^P_{inv} as

$$R\approx R_1(T-T^P_{inv}). \tag{29}$$

It then follows from Eqs. (19), (25), and (29) that the temperature dependence of P_I is given by

$$P_I=t_0R_1(T-T^P_{inv})\sqrt{T_{A\text{-}C}-T}. \tag{30}$$

Depending now on the value of T^P_{inv} relative to $T_{A\text{-}C}$, the polarity order parameter could exhibit either a monotonic increase with decreasing temperature (if $T^P_{inv}>T_{A\text{-}C}$) or a sign-inverting variation (if $T^P_{inv}<T_{A\text{-}C}$). In the latter case, the magnitude P_I starts out from zero at $T_{A\text{-}C}$ and increases continuously, on lowering the temperature, to a local maximum at $T=(2T_{A\text{-}C}-T^P_{inv})/3$, then decreases until it vanishes at T^P_{inv}, and then grows monotonically with inverted sign. Naturally, for the sign inversion to be actually observed the inversion temperature T^P_{inv} should be lower than the transition temperature $T_{A\text{-}C}$ but still within the temperature range of the Sm-C phase. If T^P_{inv} is too low, falling well outside the range of the phase, then only the first part of the sign-inverting pattern, i.e., the continuous increase toward a local maximum, is realized within the Sm-C temperature range and this behavior appears qualitatively the same as the purely noninverting behavior ($T^P_{inv}>T_{A\text{-}C}$). Altogether, according to the result obtained in Eq. (30) the different types of temperature dependence can be classified according to the value of a single characteristic parameter, the ratio $T^P_{inv}/T_{A\text{-}C}$. The various possible cases according to this classification are shown in Fig. 3.

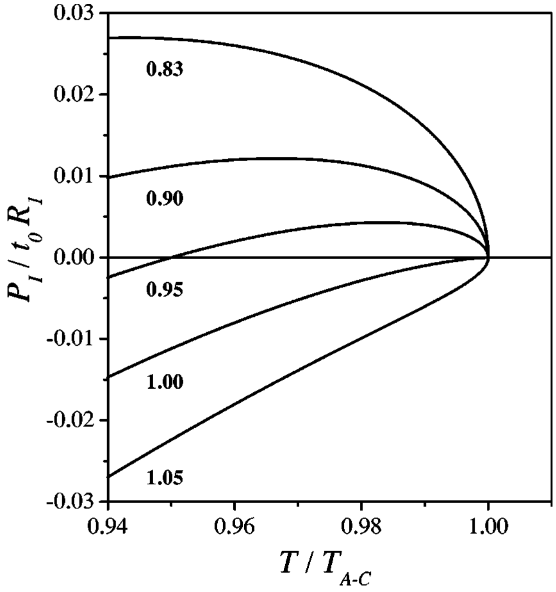

FIG. 3. Plots of the temperature dependence of the indigenous polarity order parameter P_I as calculated from Eq. (30) for different values of the ratio $T^P_{inv}/T_{A\text{-}C}$ (printed on the left-hand end of each curve).

According to the relation in Eq. (14), comparison of the predicted temperature dependence of the indigenous polarity order parameter P_I with experiment is possible in the Sm-C^* phase through measurements of the spontaneous polarization P_S. To use this relation it is necessary to specify the "transverse dipole" component $\mu^*_\perp$, and in particular its dependence on temperature. This in turn depends on the choice of the pseudovector **a** with respect to which the indigenous polarity is defined according to Eq. (13). For rigid molecules, the orientation of $\boldsymbol{\mu}$ relative to **a** will be fixed and therefore $\mu^*_\perp$ will be strictly temperature independent. For flexible molecules, the temperature dependence of $\mu^*_\perp$ will differ for different choices of **a**. In that case $\mu^*_\perp$ will be temperature independent only if **a** is taken to be fixed relative to the molecular segments to which the dipole moment $\boldsymbol{\mu}$ is attached. In any case, assuming that **a** is chosen in such a way that $\mu^*_\perp$ does not change appreciably with temperature over the range of the Sm-C^* phase, it follows from Eqs. (14) and (30) that the temperature dependence of the spontaneous polarization is of the form

$$P_S=P^0_S(T-T^P_{inv})\sqrt{T_{A\text{-}C}-T}, \tag{31}$$

where P^0_S is a temperature-independent scale factor. Figure 4 shows a comparison of the theoretical temperature dependence with experimental measurements for compounds exhibiting the temperature-inverting behavior [9] as well as for compounds with the usual monotonic variation of the spontaneous polarization [32]. The agreement is in all cases quite good and shows that the classification of the different types

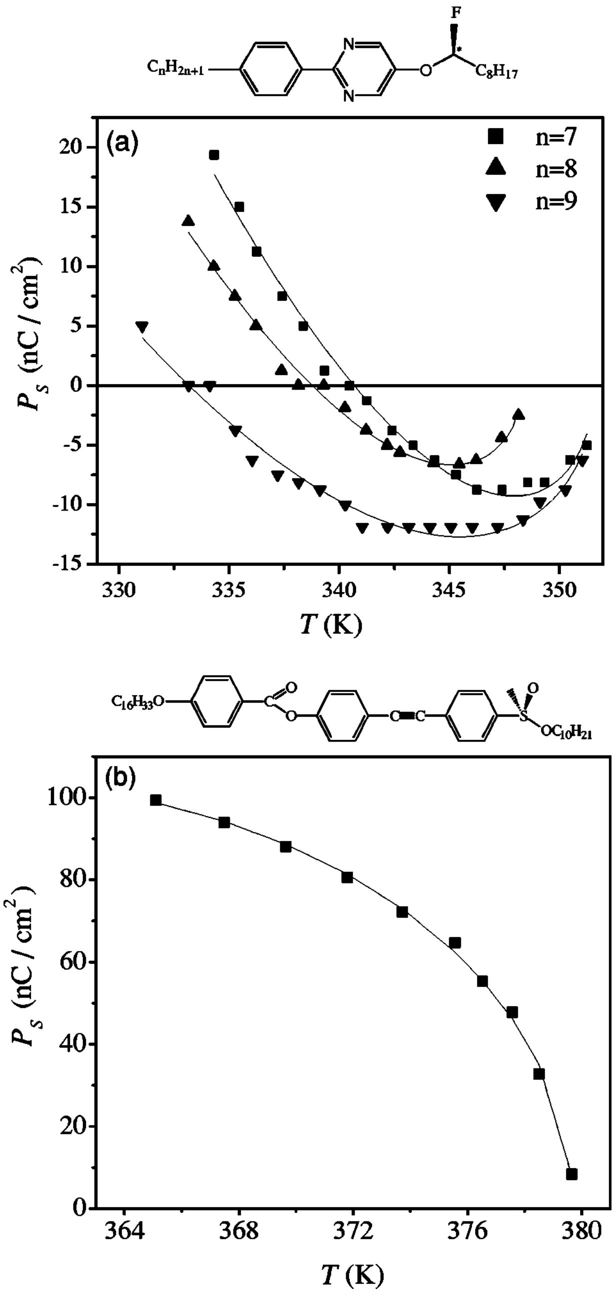

FIG. 4. Comparison of the theoretical temperature dependence of the spontaneous polarization P_S with measurement. The chemical structures of the compounds are drawn at the top of the respective graphs. The continuous lines are theoretical fits according to Eq. (31). (a) Compounds exhibiting sign inversion (experimental data from Ref. [9]). (b) Compound with the usual monotonic variation of the spontaneous polarization (experimental data from Ref. [32]). The characteristic temperature T_{inv}^{P} for this compound is below the transition temperature $T_{A\text{-}C}$ by 71 K.

of behavior of the compounds according to the single parameter $T_{inv}^{P}/T_{A\text{-}C}$ is quantitatively successful as well. Interestingly, the inversion temperature T_{inv}^{P} is found to be below the transition temperature $T_{A\text{-}C}$, both for the sign-inverting compounds and for the monotonic one. Accordingly, the sign inversion in the latter is precluded by the termination of the Sm-C^* phase at a temperature above T_{inv}^{P}. Moreover, the apparent monotonous variation in this case is due to T_{inv}^{P} being relatively far below the Sm-C^* temperature range (see the top curve in Fig. 3).

It is apparent from the structure of the sign-inverting compounds in Fig. 4(a) that the dipole moment (and chiral center) is situated right at the linkage of the mesogenic core to the chiral end-chain and its ordering is therefore affected equally strongly by the core and the tail. This is in accord with the proposed mechanism of competing couplings of the polarity to the primary and secondary tilts. Finally, it is worth noting here that the different coupling of the polarity to the primary and the secondary tilt makes it possible to differentiate the P_S response of compounds that differ with respect to the position of the transverse dipole moment within the molecular frame but are otherwise similar in structure and therefore have similar tilts.

V. SIGN INVERSION OF THE SECONDARY TILT

Analogous considerations apply to the possibility of sign inversion in the temperature dependence of the secondary tilt. By analogy to Eq. (27), the temperature dependence of the parameter r of Eqs. (18) and (21) near the transition can be expressed as

$$r \approx r_0 + r_1 (T - T_{A\text{-}C}). \tag{32}$$

If the constant r_1 is negligible compared to r_0 the ratio of tilts t'/t in Eq. (18) is temperature independent. Otherwise, an inversion temperature $T_{inv}^{t'}$ for the secondary tilt can be defined in terms of the constants r_0 and r_1:

$$T_{inv}^{t'} = T_{A\text{-}C} - r_0 / r_1. \tag{33}$$

Combining Eqs. (18), (25), and (33), the following expression is obtained for the temperature dependence of the secondary tilt near the phase transition:

$$t' = t_0 r_1 (T - T_{inv}^{t'}) \sqrt{T_{A\text{-}C} - T}. \tag{34}$$

Accordingly, if $T_{inv}^{t'}$ falls within the temperature range of the Sm-C phase the temperature dependence of the secondary tilt will exhibit a continuous sign inversion at $T_{inv}^{t'}$. On comparing Eqs. (21), (32), and (33) to the analogous set of Eqs. (22), (27), and (28), it becomes evident that the inversion temperature of the secondary tilt $T_{inv}^{t'}$ is in general different from the inversion temperature of the polarity T_{inv}^{P}. In particular, the occurrence of one type of inversion does not necessarily imply the occurrence of the other.

The vanishing and sign inversion of the secondary tilt with temperature can be related to the unwinding of the helix and subsequent winding in the opposite sense observed in some Sm-C^* compounds. This interpretation is based on the assumption that the directions of the tilt vectors in adjacent layers are correlated primarily through the direct interaction of the flexible pendant chains on either side of the interface. If then the secondary tilt t' is identified with the effective tilt order parameter of the end-chains, a sign inversion in t' will induce an inversion in the sense of the helical winding of the primary tilt vector across the smectic layers.

VI. REDUCTION TO A SINGLE TILT ORDER PARAMETER DESCRIPTION AND COMPARISON WITH THE CONVENTIONAL THEORY

The minimization of the free energy in Eq. (16) with respect to t' leads to the condition

$$a' t' = c' P_I - c'' t. \tag{35}$$

This condition can be used to eliminate the secondary tilt order parameter from the original free energy expansion. The t'-minimized expression for the free energy, obtained from Eqs. (16) and (35), has the form

$$\overline{g}_{A\text{-}C} = \frac{1}{2}\overline{a}t^2 + \frac{1}{4}bt^4 - \overline{c}P_I t + \frac{1}{2}\overline{d}P_I^2, \tag{36}$$

with

$$\begin{aligned} \overline{a} &\equiv a - (c'')^2/a', \\ \overline{c} &\equiv c - c'c''/a', \\ \overline{d} &\equiv d - (c')^2/a'. \end{aligned} \tag{37}$$

Although the reduced Landau expansion in Eq. (36) is formally an expansion in t and P_I, part of the information associated with the eliminated secondary tilt t' is implicitly contained in the "renormalized" expansion coefficients through their expressions in terms of the original coefficients as shown in Eqs. (37). In particular, as discussed in Sec. IV, the renormalized coefficients $\overline{c}$ and $\overline{d}$ could become sensitive to temperature variations around the Sm-A–Sm-C transition in spite of the relative insensitivity of the individual coefficients of the original expansion that combine to produce them. However, when the reduced expansion is considered as the starting point of the description, such sensitivity to temperature can only be introduced *ad hoc*.

Mathematically, the form of the reduced expansion is identical to the conventional Landau expansion, in its minimal form, used for the free energy of a single layer of the Sm-C^* phase [1,26–28], namely,

$$g^*_{A\text{-}C} = \frac{1}{2}at^2 + \frac{1}{4}bt^4 - CP_S t + \frac{1}{2\varepsilon_0\chi_0}P_S^2. \tag{38}$$

To a large extent, however, the resemblance is only formal as the underlying physics is different. Equation (38) describes chiral compounds; in the absence of chirality it reduces to Eq. (8). The coefficient C is assumed to be a pseudoscalar associated in some way with molecular chirality. The quadratic term in P_S is taken to represent the entropic contribution associated with the ordering of the molecular dipoles. Accordingly, in the case of achiral compounds no such contribution is allowed by the conventional theory. By contrast, the expansion of Eq. (36) takes into account the indigenous polarity and therefore admits such entropic contributions for both chiral and achiral tilted smectic phases. Since the polarity is included irrespective of molecular chirality, in the case of chiral molecules the free energy in Eq. (36) is modified only to the extent dictated by the additional interactions associated with molecular chirality and the electrostatic forces among the transverse molecular dipoles. Normally the effects of such interactions on the stability of tilted and polar ordering are estimated to be rather marginal. Thus the free energy will include a direct electrostatic contribution of the form

$$-d_{el}P_S^2 = -d_{el}(\mathcal{N}\mu_\perp^*)^2 P_I^2, \tag{39}$$

with the coefficient $d_{el} > 0$ and with the magnitude of this electrostatic term much smaller than that of the entropic term, i.e.,

$$\lambda \equiv d_{el}(\mathcal{N}\mu_\perp^*)^2/\overline{d} \ll 1. \tag{40}$$

The differences in the physics underlying the Landau expansions in Eqs. (36) and (38) have direct implications on the thermodynamics of the Sm-A–Sm-C transition. For example, ignoring all interlayer (helical structure, etc.) contributions to the free energy, Eq. (38) gives the following expression for the difference between the transition temperatures of the chiral (pure enantiomer) and achiral (racemic) phases [1]:

$$T_{A\text{-}C*} - T_{A\text{-}C} = (\varepsilon_0\chi_0/a_0)C^2, \tag{41}$$

where the temperature dependence of the parameter a, near the phase transition, is taken to be $a \approx a_0(T - T_0)$. The result obtained for this difference from the reduced expansion of Eq. (36) is

$$T_{A-C*} - T_{A\text{-}C} = (\overline{c^2}/\overline{d})[\lambda/(1-\lambda)], \tag{42}$$

and is essentially proportional to the rather small relative contribution λ of the electrostatic interactions associated with the molecular dipole moment components that survive as a result of the chiral asymmetry of the molecules. The smallness of the predicted temperature shift is in agreement with the rather small values generally obtained from measurements on enantiomeric mixtures [33,34]. For a direct quantitative comparison, however, it would be necessary to take into account the contributions associated with the helical winding of the director across the smectic layers of the chiral phase.

It has been suggested [16] that an additional, higher order, "piezoelectric" term $C' P_S t^3$ should be included in Eq. (38) in order to account for the sign-inverting temperature dependence of P_S in the context of the conventional Landau expansion. The resulting free energy expansion leads to the following dependence of the spontaneous polarization on the tilt:

$$\frac{P_S}{t} = \varepsilon_0\chi_0(C - C' t^2). \tag{43}$$

Accordingly, P_S would undergo a sign inversion at a temperature at which t^2 became equal to C/C'. For sign inversion to occur it is therefore required that C and C' be of the same sign (in the convention used here) and that $C' \gg C$, since the expansion is valid for small t^2. Thus the conventional description implies that the sign-inverting compounds belong to a class where, for some reason, the lower order piezoelectric coefficient C is much weaker than the higher order one C', i.e., to a class of compounds that are in marked contrast with the normally assumed ascending relative significance of higher order expansion terms near the phase transition.

Under these conditions for C and C', the temperature dependence for the spontaneous polarization in the case of a second order Sm-A–Sm-C^* phase transition is of the form

$$P_S \sim (T - T^*_{inv})\sqrt{T_{A\text{-}C} - T}, \qquad (44)$$

with the inversion temperature parameter given by

$$T^*_{inv} = T_{A\text{-}C} - C/C' a_0 (b + 4CC' \varepsilon_0 \chi_0). \qquad (45)$$

It is apparent, on comparing Eq. (44) with Eq. (31), that the conventional Landau expansion with higher order piezoelectric contributions and the extended expansion in Eq. (16), using the indigenous polarity and the secondary tilt, lead to functionally identical forms for the temperature dependence of P_S. Each form is parametrized by the transition temperature T_{A-C} and an inversion temperature. However, the underlying physical picture is different and the inversion temperatures are related to physically different expansion coefficients: T^P_{inv} of Eq. (31) is related to the coupling of the indigenous polarity to the primary and secondary tilts and applies to both chiral and achiral molecules, whereas T^*_{inv} applies only to chiral molecules and is related to the piezoelectric coefficients C and C'.

Finally, on further minimizing the free energy in Eq. (36) with respect to P_I, the indigenous polarity order parameter can be eliminated from the expression of the minimized free energy, yielding an expansion in only the primary tilt order parameter t. This expansion has the same form as the conventional expansion in Eq. (8). However, the renormalized coefficients in the (t', P_I)-minimized expansion are functions of the coefficients of the initial expansion of Eq. (16) rather than "starting" coefficients as in Eq. (8).

VII. DISCUSSION AND CONCLUSIONS

We have shown that the conventional phenomenological description of the Sm-A–Sm-C phase transition in terms of a single tilt order parameter is applicable only to molecules that have an axis of higher than twofold rotational symmetry. Such molecular symmetry requirements, however, are not met by any of the real molecules forming Sm-C phases. We have also shown that the symmetries and the conformational structure of the real molecules give rise to several, mutually independent, tilt order parameters and also to polar arrangement of the molecules. The latter is described by pseudovector "indigenous polarity" order parameters and is shown to be compatible with the symmetries of the achiral Sm-C phase as well as of the chiral Sm-C^*.

A phenomenological Landau expansion in terms of two tilt order parameters (primary and secondary) and of an indigenous polarity order parameter P_I is shown to describe consistently the Sm-A–Sm-C transition and the appearance of spontaneous electric polarization P_S in the chiral Sm-C^*. The relation of P_S to P_I is established by means of a well defined molecular quantity $\mu^*_\perp$ that quantifies the chirality of the electrostatic profile of the molecule. The derived temperature dependence of the spontaneous polarization involves a single characteristic reduced temperature $T^P_{inv}/T_{A\text{-}C}$ whose value differentiates between the compounds showing the usual monotonic variation of the spontaneous polarization with temperature and those exhibiting a sign-inverting variation. Temperature dependence measurements on both types of compound are accounted for very accurately.

On the phenomenological level, the sign inversion of P_S is obtained as a result of competition between the coupling of the indigenous polarity to the primary tilt order parameter and to the secondary one. On the molecular level, the implications of this competition are compatible with the picture of competing molecular conformations with opposite contributions to the spontaneous polarization. They do not exclude, however, the picture of competing intermolecular interactions, particularly if the conformational changes substantially affect the global structure of the molecule, not just the part that contributes to the spontaneous polarization.

A similar sign-inverting behavior is found possible for the secondary tilt order parameter and can be related to the inversion of the helical pitch. In the underlying molecular picture the secondary tilt is associated with the tail segments, which essentially control the interlayer correlations of the primary tilt.

This description differs from the conventional one mainly in that it recognizes that (i) polar ordering is present in the tilted smectic phase and is not a result of chirality and (ii) the tilted ordering is not always adequately described in terms of a single order parameter. On eliminating, by minimization of the free energy, the secondary tilt and the indigenous polarity order parameter, the extended Landau expansion reduces to the conventional form of the expansion for the Sm-A to Sm-C (or Sm-C^*) transition but with different physical content for the expansion coefficients.

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APPENDIX A

The purpose of this appendix is to identify different sets of independent order parameters describing tilt and polarity and to determine the relations among such sets. This is done

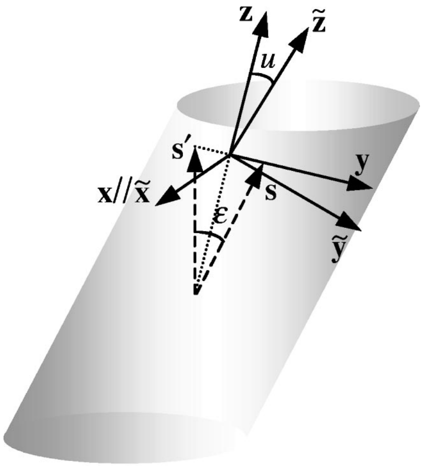

FIG. 5. Graphic representation of the molecular vectors, axis frames, and angles introduced in Eqs. (A1) and (A8) in relation to the oblique cylinder geometry.

for rigid molecules possessing a plane of symmetry and a twofold rotation axis perpendicular to it. For concreteness, we use the molecular geometry in Fig. 1(c), i.e., molecules whose orientation can be described completely in terms of two noncollinear unit vectors **s** and **s**′ lying on the plane of symmetry of the molecule and forming a fixed angle ε (see Fig. 5). As explained in Sec. II B, the relevant orientational order parameters up to second rank for such molecules are $\eta_{ab}^{(s)}, \eta_{ab}^{(s')}, \eta_{ab}^{(s,s')}$, and $\langle a_x \rangle$ and they are given in Eqs. (9)–(12).

We define an orthogonal frame of molecular axes xyz such that x coincides with the twofold symmetry axis and the unit vectors along the other two axes are related to **s** and **s**′ as follows:

$$\mathbf{z} = (\mathbf{s} + \mathbf{s}')/2\cos(\varepsilon/2), \tag{A1}$$

$$\mathbf{y} = (\mathbf{s} - \mathbf{s}')/2\sin(\varepsilon/2).$$

By analogy then with the order parameters in Eqs. (9)–(11) we can define the order parameters associated with the unit vectors of the molecular frame:

$$\eta_{ab}^{(z)} = (3\langle z_a z_b \rangle - \delta_{ab})/2,$$

$$\eta_{ab}^{(y)} = (3\langle y_a y_b \rangle - \delta_{ab})/2, \tag{A2}$$

$$\eta_{ab}^{(y,z)} = 3\langle z_a y_b + y_a z_b \rangle/4.$$

The polar order parameter $\langle a_x \rangle$ is expressed in terms of the molecular axes as

$$\langle a_X \rangle = \sin\varepsilon \langle (\mathbf{z} \times \mathbf{y})_X \rangle = -\sin\varepsilon \langle x_X \rangle. \tag{A3}$$

The second rank order parameters associated with the vectors **s**,**s**′ can be obtained from the corresponding order parameters of the molecular frames according to the relations

$$\eta_{ab}^{(s)} = \cos^2(\varepsilon/2)\,\eta_{ab}^{(z)} + \sin^2(\varepsilon/2)\,\eta_{ab}^{(y)} + \sin\varepsilon\,\eta_{ab}^{(y,z)},$$

$$\eta_{ab}^{(s')} = \cos^2(\varepsilon/2)\,\eta_{ab}^{(z)} + \sin^2(\varepsilon/2)\,\eta_{ab}^{(y)} - \sin\varepsilon\,\eta_{ab}^{(y,z)}, \tag{A4}$$

$$\eta_{ab}^{(s,s')} = \cos^2(\varepsilon/2)\,\eta_{ab}^{(z)} - \sin^2(\varepsilon/2)\,\eta_{ab}^{(y)}.$$

Now, if we describe the orientation of the molecular frame xyz relative to the macroscopic, phase fixed, frame XYZ by the three Euler angles [35] ϕ, ϑ, ψ, the relevant tilt and polarity order parameters associated with the molecular axis frame are given by

$$\eta_{YZ}^{(z)} = -\langle \sin 2\vartheta \cos\phi \rangle/2,$$

$$\eta_{YZ}^{(y)} = \langle \sin 2\vartheta \cos\phi \cos^2\psi - \sin\vartheta \sin\phi \sin 2\psi \rangle/2, \tag{A5}$$

$$\eta_{YZ}^{(yz)} = \langle \cos 2\vartheta \cos\phi \cos\psi - \cos\vartheta \sin\phi \sin\psi \rangle/2,$$

$$\langle x_X \rangle = \langle \cos\vartheta \sin\phi \sin\psi - \cos\phi \cos\psi \rangle/2.$$

It is apparent from these equations that the four order parameters are, in general, independent. In the special case where the ψ rotations are completely unbiased (higher than twofold rotational symmetry about the molecular z axis), only one independent tilt order parameter survives since then Eqs. (A5) yield

$$\eta_{YZ}^{(y)} = -\eta_{YZ}^{(z)}/2 \tag{A6}$$

and

$$\eta_{YZ}^{(yz)} = 0 = \langle x_X \rangle. \tag{A7}$$

In the general case, it is always possible to eliminate the "mixed" order parameter $\eta_{YZ}^{(yz)}$ by rotating the molecular frame about the x axis by an angle u to the molecular frame of the principal molecular axes $\tilde{x}, \tilde{y}, \tilde{z}$ (see Fig. 5). The angle u of rotation is given by the relation

$$\tan 2u = 2\,\eta_{YZ}^{(yz)}/(\eta_{YZ}^{(z)} - \eta_{YZ}^{(y)}). \tag{A8}$$

This rotation makes the mixed order parameter vanish and leaves the polar order parameter invariant since the axes x and $\tilde{x}$ coincide. The order parameters expressed in the two frames are related as follows:

$$\eta_{YZ}^{(z)} = \eta_{YZ}^{(\tilde{z})}\cos^2 u,$$

$$\eta_{YZ}^{(y)} = \eta_{YZ}^{(\tilde{y})}\sin^2 u,$$

$$\eta_{YZ}^{(yz)} = (\eta_{YZ}^{(\tilde{z})} - \eta_{YZ}^{(\tilde{y})})\sin 2u/2, \tag{A9}$$

$$\eta_{YZ}^{(\tilde{y}\tilde{z})} = 0,$$

$$\langle \tilde{x}_X \rangle = \langle x_X \rangle.$$

Accordingly, it is possible to replace the description in terms of three tilt order parameters (associated with the tensor components $\eta_{YZ}^{(s)}, \eta_{YZ}^{(s')}, \eta_{YZ}^{(s,s')}$) by a description in terms of just two tilt parameters (associated with $\eta_{YZ}^{(\tilde{z})}, \eta_{YZ}^{(\tilde{y})}$) and a molecular axis rotation angle u. The polar order parameter is identical in both descriptions.

APPENDIX B

Here we derive Eq. (14) for molecules of the idealized structure shown in Fig. 1(d). The spontaneous polarization $\mathbf{P}_S$ is related to the ensemble average of the molecular dipole moment $\boldsymbol{\mu}$ according to [1]

$$\mathbf{P}_S = \mathcal{N}\langle \boldsymbol{\mu} \rangle. \tag{B1}$$

where $\mathcal{N}$ is the molecular number density. To relate the ensemble average $\langle \boldsymbol{\mu} \rangle$ to the appropriate order parameters we express $\boldsymbol{\mu}$ in the molecular frame defined by the two vectors $\mathbf{s}, \mathbf{s}'$ of Fig. 1(d):

$$\boldsymbol{\mu} = \alpha \mathbf{s} + \beta \mathbf{s}' + \gamma (\mathbf{s} \times \mathbf{s}'), \tag{B2}$$

where

$$\alpha = [(\boldsymbol{\mu} \cdot \mathbf{s}) - (\boldsymbol{\mu} \cdot \mathbf{s}')\cos \varepsilon]/\sin^2 \varepsilon,$$

$$\beta = [(\boldsymbol{\mu} \cdot \mathbf{s}') - (\boldsymbol{\mu} \cdot \mathbf{s})\cos \varepsilon]/\sin^2 \varepsilon, \tag{B3}$$

$$\gamma = [\boldsymbol{\mu} \cdot (\mathbf{s} \times \mathbf{s}')]/\sin^2 \varepsilon,$$

and ε is the angle formed by the vectors $\mathbf{s}$, $\mathbf{s}'$ as shown in Fig. 5.

Since the molecules are assumed to be rigid, i.e., the dipole moment is fixed relative to the vectors $\mathbf{s}, \mathbf{s}'$ and the latter are fixed relative to each other, the ensemble average $\langle \boldsymbol{\mu} \rangle$ can be expressed as follows:

$$\langle \boldsymbol{\mu} \rangle = \alpha \langle \mathbf{s} \rangle + \beta \langle \mathbf{s}' \rangle + \gamma \langle (\mathbf{s} \times \mathbf{s}') \rangle. \tag{B4}$$

As explained in Sec. II, $\langle \mathbf{s} \rangle = 0 = \langle \mathbf{s}' \rangle$ due to the symmetries of the Sm-*C* phase. Furthermore, noting that $(\mathbf{s} \times \mathbf{s}') = \mathbf{a}$ and therefore $\sin \varepsilon = |\mathbf{a}|$, the ensemble average in Eq. (B4) can be written as

$$\langle \boldsymbol{\mu} \rangle = \gamma \langle (\mathbf{s} \times \mathbf{s}') \rangle = (\boldsymbol{\mu} \cdot \mathbf{a}) \langle \mathbf{a} \rangle / |\mathbf{a}|^2 = [(\boldsymbol{\mu} \cdot \mathbf{a})/|\mathbf{a}|]\mathbf{P}_I, \tag{B5}$$

where the last equality follows from the definition of the indigenous polarity in Eq. (13). On substituting this expression in Eq. (B1) and defining $\mu_\perp^* \equiv (\boldsymbol{\mu} \cdot \mathbf{a})/|\mathbf{a}|$ we obtain Eq. (14).

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