Spontaneous polarization in chiral biaxial liquid crystals

Lech Longa

Institute of Physics, Jagellonian University, Reymonta 4, Kraków, Poland
and Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57,
D-7000 Stuttgart 80, Federal Republic of Germany

Hans-Rainer Trebin

Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57,
D-7000 Stuttgart 80, Federal Republic of Germany

A phenomenological theory of polar structures in chiral biaxial liquid crystals is constructed exploiting the properties of a symmetric and traceless tensor order parameter field $Q_{\alpha\beta}(\mathbf{r})$ and of a polar field $P_\alpha(\mathbf{r})$. Full advantage is taken of the symmetry of the order parameters by systematic use of the method of integrity bases, which allows us to establish an expansion of the most general SO(3)-invariant free-energy density to arbitrary powers in the components $Q_{\alpha\beta}$ and P_α. A coordinate-independent parametrization of the invariants is introduced that yields a classification of local polar structures and some predictions about possible topologies of phase diagrams without the necessity of performing numerical calculations. As one prominent result, the theory predicts a polar, chiral biaxial state that exists due to a piezoelectric coupling of a chiral biaxial tensor field and the polarization field and which disappears if tensor is uniaxial. We then provide a general theory of flexopolarization in biaxial systems. A general biaxial system is described by 12 fundamental flexopolarization modes. Special cases, obtained by imposing symmetry restrictions to the tensor field $\mathbf{Q}$, reduce the number of modes. Finally, the theory is applied to chiral phases. Simple polar chiral structures including cholesteric and smectic-C^* liquid crystals are analyzed. In particular, it is shown that if the smectic-C^* phase is stabilized due to the piezoelectric coupling between $\mathbf{Q}$, $\mathbf{P}$, and a density wave, then it must be described as a biaxial uniform spiral with at least two nonvanishing commensurate harmonics. The minimization of the quadratic part of the Landau–de Gennes energy supplemented by (flexo)polarization terms may give rise to incommensurate two- or three-dimensional polar structures that can be stabilized by cubic terms.

I. INTRODUCTION

The transition between phases of different symmetry is described in terms of an order parameter representing the extent to which the average configuration of the molecules in the less symmetrical phase differs from that in the more symmetrical one.[1] In general, many order parameters are needed to characterize the orientational properties of a liquid crystal.[2-4] However, from a set of order parameters we may always select primary ones which govern the others. A standard way of determining these primary order parameters is to analyze the one-particle distribution function or the macroscopic response functions of the material, such as the dielectric permittivity or the diamagnetic susceptibility.[3,4] The approach based on response functions is quite attractive as it makes phenomenological theories independent of assumptions about the constituent molecules.[4(c)]

Consider, for instance, the relation between the magnetic moment $\mathbf{M}$ (due to the molecular diamagnetism) and the magnetic field $\mathbf{H}$:

$$M_\alpha = \chi_{\alpha\beta} H_\beta, \quad \alpha, \beta = x, y, z$$

where $\chi_{\alpha\beta}$ are the Cartesian components of the symmetric susceptibility tensor χ. In the isotropic phase it has a simple diagonal form,

$$\chi_{\alpha\beta} = \chi_0 \delta_{\alpha\beta} . \tag{1a}$$

Here $\delta_{\alpha\beta}$ is the Kronecker symbol. Thus the tensor order parameter $\mathbf{Q}$ is defined with elements

$$Q_{\alpha\beta} = \Delta\chi_{\alpha\beta} / \Delta\chi_{max} . \tag{1b}$$

where

$$\Delta\chi_{\alpha\beta} = \chi_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}\chi_{\gamma\gamma}$$

and where $\Delta\chi_{max}$ is the maximal anisotropy that would be observed for a perfectly ordered phase.

The standard parametrization is of the form

$$Q_{\alpha\beta} = S(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}) + b(m_\alpha m_\beta - \tfrac{1}{3}\delta_{\alpha\beta}) , \tag{1c}$$

where $\hat{\mathbf{n}}, \hat{\mathbf{m}}$ (and $\hat{\mathbf{n}} \times \hat{\mathbf{m}}$) are the orthonormal eigenvectors of $\mathbf{Q}$ corresponding to the eigenvalues $\tfrac{2}{3}S - \tfrac{1}{3}b$, $-\tfrac{1}{3}S + \tfrac{2}{3}b$, $-\tfrac{1}{3}S - \tfrac{1}{3}b$, respectively, and where the director $\hat{\mathbf{n}}$ is the eigenvector of $\mathbf{Q}$ with the largest nondegen-

erate eigenvalue.

By definition, the tensor vanishes in the isotropic phase ($S = b = 0$). In the more ordered phases (the uniaxial nematic, smectic-A, etc.) $\mathbf{Q}$ has a cylinder symmetry, i.e., $S \neq 0$, $b = 0$ or $S = 0$, $b \neq 0$, or $S = b$. This condition is written in coordinate-independent form as

$$6(\mathrm{Tr}\mathbf{Q}^3)^2 = (\mathrm{Tr}\mathbf{Q}^2)^3 . \tag{1d}$$

In the most general case $\mathbf{Q}(\mathbf{r})$ has five independent components, as $Q_{\alpha\beta} = Q_{\beta\alpha}$ and $\mathrm{Tr}\mathbf{Q} = 0$, and describes the so-called general biaxial phase.[3,4]

Note that $\mathbf{Q}$ does not include any long-range polar order, the situation encountered in most liquid crystal phases.[3] Recently, however, a considerable amount of evidence has become available that strong permanent dipole moments lead to new phenomena, like antiferroelectric smectic-A phases[5] or reentrant phase transitions.[6] Polar effects are also induced by gradients of $\mathbf{Q}$ (flexoelectric effects[7]) or by the coupling of a chiral molecular orientation field and dipole moments as in the smectic-C^* phase.[8] This evidence motivates the introduction of a secondary order parameter in the description of orientational properties of liquid crystals—namely, the polarization density $\mathbf{P}(\mathbf{r})$ of components $P_\alpha(\mathbf{r})$.

Theoretical studies of polar effects in terms of the polarization density were initiated by Meyer[7] with his assumption of shape-induced flexoelectricity in nematics. Recently, Meyer's theory was extended by Barbero et al.[9] to include effects at solid-liquid crystal interfaces.

A number of articles are also devoted to the spontaneous ferroelectricity in chiral[10] and nematics[11] systems. Out of them we particularly mention the paper by Khachaturyan,[11] which discusses the structure of a hypothetical ferroelectric nematic phase with locally helical molecular configurations and with a polarization vector parallel to the director. Although it has been recognized that, apart from $\mathbf{Q}$, a polarization field is an important order parameter in liquid crystals, no major studies of its influence have been performed so far.

Here we analyze general properties of polar liquid crystals characterized by $\mathbf{Q}$ and $\mathbf{P}$ in a systematic way. This is done by writing the phenomenological free energy in terms of an integrity basis, i.e., by a finite number of elementary tensorial polynomials through which all other tensor-valued functions are expressed as well-defined and simple products. The method of integrity bases offers *four* important advantages:

(i) Any polynomial expansion of scalar and tensorial functions is immediately available to arbitrary order in $\mathbf{Q}$ and $\mathbf{P}$,

(ii) the algebraic[12] independence of the various invariant or covariant polynomials is evident,

(iii) a natural classification is offered of possible local structures of ferroelectric liquid crystals, and

(iv) a very convenient parametrization is given of the free energy.

The organization of this paper is as follows: In Sec. II basic rules for the calculation of an integrity basis for liquid crystals along with some simple applications are provided. In Sec. III the relation between local polar structures and the integrity basis in $\mathbf{Q}$ and $\mathbf{P}$ is estab-lished. Section IV is devoted to some applications of the results of Secs. II and III. In particular, a theory of flexoelectric effects is developed for biaxial liquid crystals and polar, chiral biaxial structures, like Sm-C^*-liquid crystals, are considered. Section V contains a summary.

II. INTEGRITY BASES: SIMPLE EXAMPLES FOR LIQUID CRYSTALS

The mathematical concept of integrity bases was introduced by Molien[13] and Hilbert about a century ago to characterize the algebra of invariants of a finite group. It was shown that a finite number of (algebraically) independent invariant polynomials in the components of an irreducible representation of a finite group can be constructed (comprising the integrity basis) such that all other invariants are written as polynomials of these basic invariants. This very elegant group theoretical method has recently been extended to compact Lie groups by Judd et al.,[14(a)] Gaskell et al.[14(b)] and Bistricky et al.[14(c)] Some results for SU(2) symmetry are collected in Refs. 14.

In this section by some simple examples the theory of integrity bases is applied to the topology of phase diagrams in molecular and Landau theories of liquid crystals. For the sake of clarity, we discuss polynomials in $\mathbf{P}$ and in $\mathbf{Q}$ separately and postpone the coupling between the order parameters to Sec. III.

The discussion of the integrity basis for the symmetric and traceless tensor field $\mathbf{Q}$ and for the polarization field $\mathbf{P}$ becomes simpler if we switch from the Cartesian representation to the spherical one. The latter defines the irreducible representations of SO(3).

The spherical components of $\mathbf{Q}$ form an $L = 2$ quadrupole tensor $\mathbf{Q}^{(2)}$ with components $Q_m^{(2)}$ ($m = \pm 2, \pm 1, 0$), where

$$Q_{\pm 2}^{(2)} = -\tfrac{1}{2}(Q_{xx} - Q_{yy} \pm 2iQ_{xy}) ,$$

$$Q_{\pm 1}^{(2)} = \pm(Q_{xz} \pm iQ_{yz}) , \tag{2a}$$

$$Q_0^{(2)} = \frac{3}{\sqrt{6}}(Q_{xx} + Q_{yy}) .$$

In the spherical representation the constraints $Q_{\alpha\beta} = Q_{\beta\alpha}$, $\mathrm{Tr}\mathbf{Q} = 0$ are automatically taken notice of.

The spherical components of the vector field $\mathbf{P}$ form an $L = 1$ dipole tensor $\mathbf{P}^{(1)}$ of components $P_m^{(1)}$ ($m = \pm 1, 0$), where

$$P_\pm^{(1)} = \mp \frac{i}{\sqrt{2}}(P_x \pm iP_y) ,$$

$$P_0^{(1)} = iP_z . \tag{2b}$$

From the components $T_m^{(1)}$ and $S_q^{(k)}$ of two spherical tensors of ranks 1 and q, respectively, one can form via the standard Clebsch-Gordan coupling the $(2l + 1)(2k + 1)$ irreducible components of a product tensor transforming according to the angular momentum quantum numbers $L \in \{ l + k, l + k - 1, \ldots, |l - k| \}$

$$[\mathbf{T}^{(l)} \otimes \mathbf{S}^{(k)}]_M^{(L)} \equiv \sum_{m_1, m_2} \begin{bmatrix} l & k & L \\ m_1 & m_2 & M \end{bmatrix} T_{m_1}^{(l)} S_{m_2}^{(k)} , \tag{2c}$$

where

$$\begin{bmatrix} l & k & L \\ m_1 & m_2 & m \end{bmatrix}$$

are Clebsch-Gordan coefficients. To the product $[\mathbf{T}^{(l)} \otimes \mathbf{S}^{(k)}]^{(L)}$ one can couple a third tensor $R_s^{(p)}$ to form a spherical tensor

$$[[\mathbf{T}^{(l)} \otimes \mathbf{S}^{(k)}]^{(L)} \otimes \mathbf{R}^{(p)}]^{(K)} ,$$

etc.

An important problem is to determine all linearly independent tensors which transform according to an irreducible representation of the group SO(3) and whose components are homogeneous polynomials in $Q_m^{(2)}$ or $P_n^{(1)}$. These we denote "irreducible tensors." Note that any tensorial function, which is analytical in the components $T_m^{(l)}$ and $S_q^{(k)}$ of spherical tensors and transforms itself like a spherical harmonic L, can be written as a linear combination of irreducible tensors, transforming like the harmonic L, each. In particular, molecular, Landau, or elastic energies of liquid crystals can be viewed as linear combinations of SO(3) invariant polynomials, i.e., spherical products with total momentum $L = 0$.

The explicit form of the irreducible tensors is quickly established through an integrity basis[14] which we determine in the following way:

First we note the following theorem:[14] The total number $m_{n,J}$ of linearly independent tensorial polynomials of a given degree n, which transform according to an irreducible representation of SO(3) of momentum J, can be extracted from a generating function $\mathcal{G}(q,\Lambda)$.

This generating function is a rational expression whose numerator and denominator are polynomials in q and Λ. The power-series expansion of $\mathcal{G}(q,\Lambda)$ contains only positive integer coefficients—namely, the numbers $m_{n,J}$:

$$\mathcal{G}(q,\Lambda) = \sum_{n,J} m_{n,J} q^n \Lambda^J . \tag{3}$$

From the rational form of $\mathcal{G}$ one can derive the integrity basis as shown below.

The construction of $\mathcal{G}(q,\Lambda)$ is based on the orthogonality theorems for characters of products of irreducible representations of SU(2).[14] The generating functions for tensors of momentum $L \leq \frac{13}{2}$ are collected in Ref. 14(c). Beware, however, of a misprint in formula (2.3) of Ref. 14(c): The term $\mathbf{U}^{3L-6}$ there should read $\mathbf{A}^{3L-6}$. Detailed calculations for $L = 6$ are found in Ref. 15. Here we list the generating functions and integrity bases for vectors $(L=1)$ and for symmetric and traceless tensors $(L=2)$.

Vectors (L=1). For the vector field $\mathbf{P}^{(1)}$ the generating function $\mathcal{G}(p,\Lambda)$ reads

$$\mathcal{G}(p,\Lambda) = \frac{1}{(1-p^2)(1-p\Lambda)} \tag{4a}$$

$$= \sum_{n=0}^\infty (p^2)^n \sum_{L=0}^\infty p^L \Lambda^L . \tag{4b}$$

From the rational form of $\mathcal{G}(p,\Lambda)$ it follows[14] that polynomials in the variable $P_m^{(1)}$ exclusively, which transform

like components of an irreducible representation of SO(3), can be composed by only two tensors—namely,

$$\mathbf{I}_{1,0}^{(1)} \equiv \mathbf{P}^{(1)}$$

and

$$\mathbf{I}_{2,0}^{(0)} = [\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(0)} \equiv P^2 = \frac{1}{\sqrt{3}} P_\alpha P_\alpha ,$$

via Clebsch-Gordan coupling of $\mathbf{P}^{(1)}$ with itself to the highest possible total momentum. The resulting polynomials can additionally be multiplied by an arbitrary power of P^2 to yield

$$(P^2)^n [\cdots [[\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(2)} \otimes \mathbf{P}^{(1)}]^{(3)} \otimes \cdots]^{(m)} . \tag{4c}$$

The two basic tensorial polynomial fields $\mathbf{P}^{(1)}$ and P^2 are the integrity basis for functions in the variable $P_m^{(1)}$. Note that Clebsch-Gordan coupling to the highest possible momentum is particularly simple as the sequence of the factors is irrelevant.

Quadrupole tensors (L=2). For $\mathbf{Q}^{(2)}$ the generating function is

$$\mathcal{G}(q,\Lambda) = \frac{1+q^3\Lambda^3}{(1-q\Lambda^2)(1-q^2\Lambda^2)(1-q^2)(1-q^3)} \tag{5a}$$

$$= 1 + q\Lambda^2 + q^2(\Lambda^0 + \Lambda^2 + \Lambda^4)$$

$$+ q^3(\Lambda^0 + \Lambda^2 + \Lambda^3 + \Lambda^4 + \Lambda^6) + \cdots , \tag{5b}$$

The rational form of the generating function (4a) now provides important information about the structure of the integrity basis:[14] from the factors in denominator and numerator one reads off that the integrity basis consists of five "elementary" tensors $\mathbf{I}_{0,N}^{(L)}$, whose degrees N and momenta L are the powers of q and Λ, namely, $(N,L) = (1,2), (2,2), (2,0), (3,0), (3,3)$. These tensors can be unambiguously identified as[16]

$$\mathbf{I}_{0,1}^{(2)} \equiv \mathbf{Q}^{(2)}, \quad \mathbf{I}_{0,2}^{(2)} = [\mathbf{Q}^{(2)} \otimes \mathbf{Q}^{(2)}]^{(2)}$$

$$\mathbf{I}_{0,2}^{(0)} = [\mathbf{Q}^{(2)} \otimes \mathbf{Q}^{(2)}]^{(0)} \equiv Q^2 = \frac{1}{\sqrt{5}} \mathrm{Tr} \mathbf{Q}^2 , \tag{6a}$$

$$\mathbf{I}_{0,3}^{(0)} = [\mathbf{I}_{0,1}^{(2)} \otimes \mathbf{I}_{0,2}^{(2)}]^{(0)} = (\tfrac{12}{35})^{1/2} \mathrm{Tr} \mathbf{Q}^3 ,$$

and

$$\mathbf{I}_{0,3}^{(3)} = [\mathbf{I}_{0,1}^{(2)} \otimes \mathbf{I}_{0,2}^{(2)}]^{(3)}$$

$$= -\frac{\sqrt{5}}{\sqrt{2}} [\mathbf{Q}^{(2)} \otimes [\mathbf{Q}^{(2)} \otimes \mathbf{Q}^{(2)}]^{(4)}]^{(3)} . \tag{6b}$$

Again, any irreducible tensorial polynomial in the components of $\mathbf{Q}^{(2)}$ can be formed by all possible products of the basis tensors (6a) coupled according to Clebsch-Gordan to the highest possible total momenta. The tensor $\mathbf{I}_{0,3}^{(3)}$, Eq. (6b), associated with the term $q^3\Lambda^3$ in the numerator of Eq. (5a), can appear only linearly. A thorough discussion of this method is found in Ref. 16.

Before going to implications for physical phenomena, let us first interpret the integrity basis elements. The $\mathbf{I}_{0,2}^{(0)}$ invariant is the square of the norm of the order parameter $\mathbf{Q}^{(2)}$:

$$\mathbf{I}_{0,2}^{(0)} = |\mathbf{Q}^{(2)}|^2 \equiv Q^2 . \tag{7a}$$

The invariant $I_{0,3}^{(0)}$ is the scalar product of two members of the integrity basis-namely, $I_{0,1}^{(2)}$ and $I_{0,2}^{(2)}$. These we view as five-component vectors, and $(I_{0,3}^{(0)})^2$ as their scalar product:

$$\begin{aligned}
(I_{0,3}^{(0)})^2 &= ([I_{0,1}^{(2)} \otimes I_{0,2}^{(2)}]^{(0)})^2 \\
&= [|I_{0,1}^{(2)}||I_{0,2}^{(2)}|\cos(\phi)]^2 \\
&= \frac{2\sqrt{5}}{7} Q^6 \cos(\phi)^2 \le \frac{2\sqrt{5}}{7} Q^6 ,
\end{aligned} \tag{7b}$$

where ϕ is the "angle"[16] between vectors $I_{0,1}^{(2)}$ and $I_{0,2}^{(2)}$. The uniaxiality condition (1d) can be written in terms of $I_{0,2}^{(0)}$ and $I_{0,3}^{(0)}$ as

$$10(I_{0,2}^{(0)})^3 = 7\sqrt{5}(I_{0,3}^{0})^2 ,$$

which means that the uniaxial phase corresponds to the case of $\phi = 0$ (prolate uniaxial phase) or π (oblate uniaxial phase). Thus the value of $\cos(\phi)^2$ is a measure for the degree of uniaxiality of a given phase while the sign of $\cos(\phi)$ distinguishes between the oblate and the prolate case. A natural, coordinate-independent, parametrization of the Landau theory of nematics phases is obtained, if the integrity basis elements $I_{0,2}^{(0)}$ and $I_{0,3}^{(0)}$ are replaced by the pair $[Q, w = \cos(\phi)]$ of variables. The allowed values of $I_{0,2}^{(0)}$ and $I_{0,3}^{(0)}$ (equivalently TrQ^2 and TrQ^3 or Q and w) are depicted in Fig. 1.

The $I_{0,3}^{(3)}$ element of the integrity basis has a qualitatively different interpretation. For uniaxial phases the vectors $I_{0,1}^{(2)}$ and $I_{0,2}^{(2)}$ are either parallel ($\phi = 0$) or antiparallel ($\phi = \pi$). From Eqs. (6), (7a), and (7b) it follows that

$$I_{0,2}^{(0)} I_{0,2}^{(2)} = \pm I_{0,3}^{(0)} I_{0,1}^{(2)} . \tag{7c}$$

Consequently, for uniaxial symmetry we find

$$I_{0,3}^{(3)} = \pm \left[\frac{2\sqrt{5}}{7} \right]^{1/2} Qw [Q^{(2)} \otimes Q^{(2)}]^{(3)} = 0 , \tag{7d}$$

so that $I_{0,3}^{(3)}$ vanishes. Its norm,

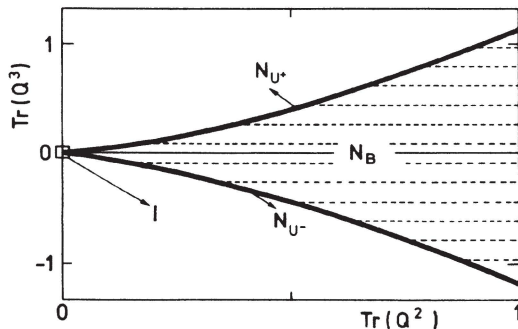FIG. 1. Allowed variation of the independent degrees of freedom TrQ^2 and TrQ^3 (shaded area) and identification of the corresponding phases.

$$\begin{aligned}
|I_{0,3}^{(3)}| &\equiv \left[[I_{0,3}^{(3)} \otimes I_{0,3}^{(3)}]^{(0)} \right]^{1/2} \\
&= \left[\frac{5\sqrt{7}}{14} \left| \frac{2\sqrt{5}}{7} (I_{0,2}^{(0)})^3 - (I_{0,3}^{(0)})^2 \right| \right]^{1/2} \\
&= \left[\frac{5\sqrt{5}}{7\sqrt{7}} Q^6 (1 - w^2) \right]^{1/2} \\
&= \frac{1}{7\sqrt{7}} [(TrQ^2)^3 - 6(TrQ^3)^2] ,
\end{aligned} \tag{7e}$$

is proportional to $[(1 - w^2)]^{1/2}$ and provides a measure of biaxiality. Maximal biaxiality is present for $w = 0$, i.e., for $I_{0,3}^{(0)} = TrQ^3 = 0$.

The deviation of Q from the uniaxial form is frequently expressed by a biaxiality parameter χ ($0 \le \chi \le 1$), defined for the diagonal form of Q,

$$[Q]_{\text{diag}} = \left[\frac{2\sqrt{5}}{3} \right]^{1/2} Q \cos \left[\frac{\phi}{3} \right]$$
$$\times \begin{bmatrix} \frac{1}{2}(-1-\chi) & 0 & 0 \\ 0 & \frac{1}{2}(-1+\chi) & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{7f}$$

where

$$\chi = \sqrt{3} \tan \left[\frac{\phi}{3} \right] , \tag{7g}$$

with $\cos(\phi) = w$ and

$$w^2 = 6(TrQ^3)^2 / (TrQ^2)^3 .$$

Now we demonstrate how the integrity-basis approach simplifies the study of topologies of phase diagrams. This subject has been extensively treated in our article on the Landau theory of the nematic-isotropic phase transition in Ref. 4(c) (see also Ref. 17), of which we repeat the most important arguments.

The internal symmetry of Q, if expressed by the invariants $I_{0,2}^{(0)}, I_{0,3}^{(0)}$ reveals (1) a first-order phase transition from the isotropic to the uniaxial nematic phase ($I \to N_U$) and (2) the existence of a biaxial nematic phase.

These statements follow from the expansion of the Landau free energy F_{bulk} in powers of $(I_{0,2}^{(0)}, I_{0,3}^{(0)}) \equiv (TrQ^2, TrQ^3)$ or (Q, w),

$$\begin{aligned}
F_{\text{bulk}} &= A \, TrQ^2 + B \, TrQ^3 + C[TrQ^2]^2 + D[TrQ^2][TrQ^3] \\
&\quad + E[TrQ^2]^3 + E'[TrQ^3]^2 + \cdots \\
&= \alpha Q^2 + \beta Q^3 w + \gamma Q^4 + \delta Q^5 w + \varepsilon Q^6 + \varepsilon' Q^6 w^2 + \cdots ,
\end{aligned} \tag{8}$$

where $-1 \le w \le 1$, $Q \ge 0$; here $A = a(T - T^*) \propto \alpha$, $B \propto \beta$, ture and T^* is the spinodal.

The minimization of expansion (8) is simple in the independent variables ($Q \ge 0$, $-1 \le w \le 1$), and even without numerical calculations the following results are obvious:

(i) For a quartic free energy [$C > 0$, $D = E = E' = 0$ in

Eq. (8)], the free energy is a linear function of w, and the minimum always is taken at the extremal values of w — namely, $+1$ for $\beta < 0$ and -1 for $\beta > 0$. Consequently, there is only one low-temperature phase, i.e., the oblate uniaxial phase (N_{U^+}) or the prolate uniaxial phase (N_{U^-}) with D_∞ symmetry, accessible from the isotropic phase through a first-order phase transition, if $B \neq 0$, or, if $B = 0$, a continuous transition at the Landau point $(A = B = 0)$.

(ii) The biaxial phase N_B of symmetry D_2 can be a minimum of the free energy provided at least one term proportional to w^2 is present $(E' \neq 0)$. For the expansion to be positive definite ("stable") in the absence of higher-order terms it is required that $E > 0$ and $E' > 0$.

In spite of the known limitations of the Landau theory, the conclusions from Eq. (8) agree with experiment.[4(c)] All observed nematic phases[4(c),18] are classified properly and the topologies of phase diagrams are reproduced correctly.[4(c)18] As the Landau theory is phenomenological, it contains several free parameters. These can, in principle, be fitted to various experimental data[19] and provide a semiquantitative description of order parameter, specific heat, entropy, etc. Some of these parameters even have a simpler molecular interpretation. In particular, the parameter B measures molecular flatness, being positive for the rodlike molecules and negative for disk-like ones as for these signs the minimum of the quartic free energy is obtained for a prolate and an oblate tensor order parameter [see (i) and (ii) above and Fig. 1]. Analogously, the coefficient E' is a measure for the deviation of an averaged molecular shape from axial symmetry, i.e., of intrinsic (molecular) biaxiality.

III. INTEGRITY BASIS FOR POLAR LIQUID CRYSTALS

In Sec. II we have demonstrated how to construct all linearly independent, irreducible tensors built out of $\mathbf{Q}^{(2)}$

and $\mathbf{P}^{(1)}$ separately. Here we concentrate on polar nematic liquid crystals described by a free energy, which is polynomial in both $\mathbf{Q}^{(2)}$ and $\mathbf{P}^{(1)}$. A similar analysis could, in principle, be applied to an expansion into any set of tensors transforming according to one or several irreducible representations of a compact Lie group.

In order to establish the integrity basis for irreducible tensorial polynomials in two order parameters $\mathbf{P}^{(1)}$ and $\mathbf{Q}^{(2)}$, we first construct the generating function $\mathcal{G}(q,p,\Lambda)$ with the help of those for vector $(L = 1)$ and tensor $(L = 2)$ fields of Sec. II [see Eqs. (4a) and (5a)]. The function

$$\mathcal{F}(\Lambda_1, \Lambda_2, \Lambda) = [(1 - \Lambda_1^{1/2}\Lambda^{1/2})(1 - \Lambda_2^{1/2}\Lambda^{1/2})$$

$$\times (1 - \Lambda_1^{1/2}\Lambda_2^{1/2})]^{-1}$$

$$= 1 + \Lambda_1^{1/2}\Lambda^{1/2} + \Lambda_2^{1/2}\Lambda^{1/2}$$

$$+ \Lambda_1^{1/2}\Lambda_2^{1/2}(1 + \Lambda) + \cdots \qquad (9a)$$

is a generating function for the SU(2) Clebsch-Gordan series in the following sense: The presence of the term $\Lambda_1^l \Lambda_2^m \Lambda^n$ indicates that the tensor product of two SU(2) representations of the momenta l and m contains the representation of momentum n. If we now multiply the generating functions $\mathcal{G}(p, \Lambda_1)$ for $\mathbf{P}^{(1)}$ and $\mathcal{G}(q, \Lambda_2)$ for $\mathbf{Q}^{(2)}$ by the generating function $\mathcal{F}(\Lambda_1^{-1}, \Lambda_2^{-1}, \Lambda)$ and retain only the terms not containing Λ_1 and Λ_2, we obtain the generating function for linearly independent polynomials in the components of two irreducible tensors of momenta 1 and 2, which transform according to components of irreducible representations of SO(3). Explicitly (we replace Λ_i, Λ by Λ_i^2, Λ^2 to avoid noninteger exponents,

$$\mathcal{G}(p, q, \Lambda^2) = \mathcal{P}^0_{\Lambda_1 \Lambda_2}\{\mathcal{G}(p, \Lambda_1^2, L = 1)\mathcal{F}(\Lambda_1^{-2}, \Lambda_2^{-2}, \Lambda^2)\mathcal{G}(q, \Lambda_2^2, L = 2)\} ,$$

$$= \frac{1}{(1 - q^2)(1 - q^3)(1 - p^2)}$$

$$\times \left[\sum_{\substack{n_1, \ldots, n_6 = 0 \\ 2n_1 - n_2 - n_4 = 0 \\ -n_3 - n_4 + 4n_5 + 4n_6 = 0}}^{\infty} \Lambda^{n_2 + n_3} p^{n_1} q^{n_5 + 2n_6} + \sum_{\substack{n_1, \ldots, n_6 = 0 \\ 2n_1 - n_2 - n_4 = 0 \\ 6 - n_3 - n_4 + 4n_5 + 4n_6 = 0}}^{\infty} \Lambda^{n_2 + n_3} p^{n_1} q^{n_5 + 2n_6 + 3} \right] , \qquad (9b)$$

where $P^0_{\Lambda_1 \Lambda_2 \Lambda}\{ \cdots \}$ means the part of the expansion in brackets that is independent of Λ_1 and Λ_2. For invariants composed of $P_m^{(1)}$ and $Q_n^{(2)}$ we get

$$\mathcal{G}(p, q) = \frac{1 + p^3 q^3}{(1 - q^2)(1 - q^3)(1 - p^2)(1 - p^2 q)(1 - p^2 q^2)} . \qquad (9c)$$

The generating function (9c) for invariants of both $\mathbf{P}^{(1)}$ and $\mathbf{Q}^{(2)}$ has a form similar to the one for $\mathbf{Q}^{(2)}$ [Eq. (5a)]. Here, however, the interpretation of the terms is different. It may be interpreted in terms of six basic invariants $I_{\alpha\beta}^{(0)}$, $(\alpha, \beta) = (0, 2)$, $(0, 3)$, $(2, 0)$, $(2, 1)$, $(3, 3)$, of degree α and β in the components of $\mathbf{P}^{(1)}$ and $\mathbf{Q}^{(2)}$, respectively. The invariants in the spherical and Cartesian form are identified as

$$\mathbf{I}_{0,2}^{(0)} \equiv Q^2 = \frac{1}{\sqrt{5}} \mathrm{Tr} \mathbf{Q}^2, \quad \mathbf{I}_{0,3}^{(0)} = \left[\frac{2\sqrt{5}}{7} \right]^{1/2} Q^3 w = (\tfrac{12}{35})^{1/2} \mathrm{Tr} \mathbf{Q}^3 \; ,$$

$$\mathbf{I}_{2,0}^{(0)} = [\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(0)} \equiv P^2 = \frac{1}{\sqrt{3}} P_\alpha P_\alpha \; , \tag{10a}$$

$$\mathbf{I}_{2,1}^{(0)} = [[\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(2)} \otimes \mathbf{I}_{0,1}^{(2)}]^{(0)} \equiv [\mathbf{P}^{(2)} \otimes \mathbf{I}_{0,1}^{(2)}]^{(0)}$$

$$\equiv |\mathbf{P}^{(2)}| \, |\mathbf{I}_{0,1}^{(2)}| \cos\phi_1 = \left[\frac{2\sqrt{5}}{5} \right]^{1/2} P^2 Q w_1$$

$$= \frac{1}{\sqrt{5}} P_\alpha Q_{\alpha\beta} P_\beta = \frac{1}{\sqrt{5}} \{ S[(\mathbf{P}\cdot\hat{\mathbf{n}})^2 - \tfrac{1}{3} P_\alpha P_\alpha] + b[(\mathbf{P}\cdot\hat{\mathbf{m}})^2 - \tfrac{1}{3} P_\alpha P_\alpha] \} \; ,$$

$$\mathbf{I}_{2,2}^{(0)} = [[\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(2)} \otimes \mathbf{I}_{0,2}^{(2)}]^{(0)} \equiv [\mathbf{P}^{(2)} \otimes \mathbf{I}_{0,2}^{(2)}]^{(0)}$$

$$= |\mathbf{P}^{(2)}| \, |\mathbf{I}_2^{(2)}| \cos\phi_2 = \frac{2}{\sqrt{7}} P^2 Q^2 w_2$$

$$= (\tfrac{12}{35})^{1/2} [P_\alpha Q_{\alpha\beta}^2 P_\beta - \tfrac{1}{3} \mathrm{Tr}(\mathbf{Q}^2) P_\alpha P_\alpha]$$

$$= (\tfrac{12}{35})^{1/2} [\tfrac{1}{3}(S^2 - 2Sb)(\mathbf{P}\cdot\hat{\mathbf{n}})^2 + \tfrac{1}{3}(b^2 - 2Sb)(\mathbf{P}\cdot\hat{\mathbf{m}})^2$$

$$- \tfrac{1}{9}[(S-b)^2 - 2Sb] P_\alpha P_\alpha \}$$

and

$$\mathbf{I}_{3,3}^{(0)} = [[\mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)} \otimes \mathbf{P}^{(1)}]^{(3)} \otimes \mathbf{I}_{0,3}^{(3)}]^{(0)} \equiv [\mathbf{P}^{(3)} \otimes \mathbf{I}_{0,3}^{(3)}]^{(0)}$$

$$= |\mathbf{P}^{(3)}| \, |\mathbf{I}_{0,3}^{(3)}| \cos\phi_3 = \frac{[6\sqrt{15}(1-w^2)]^{1/2}}{7} P^3 Q^3 w_3$$

$$= -\frac{2\sqrt{3}}{7} P_\alpha P_\beta P_\gamma \varepsilon_{\alpha\mu\nu} Q_{\mu\beta} Q_{\nu\gamma}^2$$

$$= -\frac{2\sqrt{3}}{7} [Sb(S-b)(\mathbf{P}\cdot\hat{\mathbf{n}})(\mathbf{P}\cdot\hat{\mathbf{m}})(\mathbf{P}\cdot[\hat{\mathbf{n}}\times\hat{\mathbf{m}}])] \; , \tag{10b}$$

where

$$|\mathbf{P}^{(2)}|^2 = \frac{2\sqrt{5}}{5} P^4, \quad |\mathbf{P}^{(3)}|^2 = \frac{6\sqrt{21}}{35} P^6 \; , \tag{10c}$$

and where we have introduced angles ϕ_α, $\alpha = 1,2,3$, between the "vectors" $\mathbf{P}^{(1)}$ and $\mathbf{I}_{n,j}^{(m)}$ of cosines $w_\alpha = \cos(\phi_\alpha)$. Any other invariant formed by coupling of $\mathbf{P}^{(1)}$ and $\mathbf{Q}^{(2)}$ can be expressed as a polynomial of invariants (10a) and (10b) in which the invariant (10b) appears linearly, at most. The powers $(\mathbf{I}_{3,3}^{(0)})^n$, with $n > 1$, are polynomials of (10a). In particular, one finds

$$(\mathbf{I}_{33})^2 = -\frac{5\sqrt{3}\sqrt{5}}{14} \mathbf{I}_{02} \mathbf{I}_{20} (\mathbf{I}_{22})^2 + \frac{25\sqrt{3}\sqrt{7}}{49} \mathbf{I}_{02} (\mathbf{I}_{21})^2 \mathbf{I}_{22} - \frac{25\sqrt{3}}{49} (\mathbf{I}_{02})^2 (\mathbf{I}_{21})^2 \mathbf{I}_{20} + \frac{10\sqrt{3}\sqrt{5}}{147} (\mathbf{I}_{02})^3 (\mathbf{I}_{20})^3$$

$$- \frac{50\sqrt{3}\sqrt{7}}{147} \mathbf{I}_{03} (\mathbf{I}_{21})^3 + \frac{5\sqrt{3}\sqrt{5}}{7} \mathbf{I}_{03} \mathbf{I}_{21} \mathbf{I}_{22} \mathbf{I}_{20} - \frac{5\sqrt{3}}{21} (\mathbf{I}_{03})^2 (\mathbf{I}_{20})^3 - \frac{5\sqrt{3}\sqrt{5}\sqrt{7}}{42} (\mathbf{I}_{22})^3 \; , \tag{10d}$$

where $\mathbf{I}_{ij}$ stands for $\mathbf{I}_{i,j}^{(0)}$. For $P \neq 0$ and $Q \neq 0$ relation (10d) is reduced to one between the cosines w, w_α ($\alpha = 1,2,3$)

$$5 + 30 w w_1 w_2 + 30 w_1^2 w_2 - 5w^2 - 20 w w_1^3 - 15 w_1^2$$

$$- 10 w_2^3 - 15 w_2^2 - 9(1-w^2) w_3^2 = 0 \; . \tag{10e}$$

Equations (10d) and (10e) demonstrate that the variables w, w_α are not independent.

Further nonpolynomial relations between w, w_1, w_2, and w_3 are expected because the tensor field $\mathbf{P}^{(2)}$ in $\mathbf{I}_{21}$ and $\mathbf{I}_{22}$, Eqs. (10), is a product of $\mathbf{P}^{(1)}$ with itself and thus not the most general tensor transforming according to $L = 2$.

The exact range of values for w, w_1, w_2, and w_3 has been calculated in the parametrization (1c) for $Q_{\alpha\beta}$ and with P_α decomposition of $\mathbf{P}$ in a right-handed Cartesian coordinate system $(\hat{\mathbf{m}}, \hat{\mathbf{n}} \times \hat{\mathbf{m}}, \hat{\mathbf{n}})$ parallel to the eigenvec-

tor tripod of $Q_{\alpha\beta}$. We obtain

$$w = \frac{(\eta-2)(\eta+1)(2\eta-1)}{2(\eta^2-\eta+1)^{3/2}} \ , \tag{11a}$$

$$w_1 = \frac{3s_t(1-\eta-s_f)+2\eta-1}{2(\eta^2-\eta+1)^{1/2}} \ , \tag{11b}$$

$$w_2 = \frac{3s_t[1-\eta^2+s_f(2\eta-1)]+2\eta^2-2\eta-1}{2(\eta^2-\eta+1)} \ , \tag{11c}$$

$$(1-w^2)w_3^2 = \frac{405(\eta-1)\eta^2(s_f-1)s_f(s_t-1)s_t^2}{4(\eta^2-\eta+1)^3} \ , \tag{11d}$$

where $\eta = S/b$ $(-\infty < \eta < +\infty)$, $s_t = [\sin(\Theta)]^2$, $s_f = [\sin(\Phi)]^2$, Θ is the angle between $\hat{n}$ and $\mathbf{P}$, and Φ is the angle between $\hat{m}$ and the projection of $\mathbf{P}$ onto the $(\hat{m}, \hat{n}\times\hat{m})$ plane.

Analyzing Eqs. (11), we can state that w_1, w_2, and w belong to a three-dimensional volume Ω, embedded in a cube (w_1, w_2, w) of edge length 2. A cross section of Ω for constant w, Fig. 2, is a triangle (shaded in Fig. 2) whose sides fulfill the equation

$$w_2 = Aw_1 + (1-A^2)/2 \ , \tag{12a}$$

with three different values of A, which are the roots of the equation

$$w = A(3-A^2)/2, \quad |A| < 2 \ . \tag{12b}$$

In the limiting case of $w=1(-1)$ the triangle degenerates to an interval $w_2 = w_1$ $(-w_1)$ where $-0.5 \leq w_1 \leq 1(-1 \leq w_1 \leq 0.5)$. All points on the surface $\partial\Omega$ of Ω satisfy the condition $w_3(\partial\Omega) = 0$. The transformation $(w, w_1) \leftrightarrow (-w, -w_1)$ leaves Eq. (10e) and hence also Ω unchanged and expresses a symmetry between oblate and prolate states.

The projection of Ω onto the (w_1, w_2) plane, Fig. 3, is an area enclosed by two parabolas,

$$2w_1^2 - 1 \leq w_2 \leq \tfrac{1}{2}(w_1^2+1) \ . \tag{12c}$$

The parabola $D'CD$, Figs. 2 and 3, is given by projecting the edges

$$\{w, w_1, w_2\} = \{4w_1^3 - 3w_1, w_1, 2w_1^2 - 1\} \tag{12d}$$

and

$$\{w, w_1, w_2\} = \left\{\frac{3w_1-w_1^3}{2}, w_1, \frac{w_1^2+1}{2}\right\} \tag{12e}$$

onto the (w_1, w_2) plane (remember that in all these cases w_3 is zero). For nonzero w_3, i.e., for a position (w, w_1, w_2) in the interior of Ω, the value of w_3^2 is found by Eq. (10e).

The relations (10) induce inequalities between the invariants in Cartesian form which we list here for completeness:

$$6(\mathrm{Tr}\mathbf{Q}^3)^2 \leq (\mathrm{Tr}\mathbf{Q}^2)^3 \ ,$$

$$3(P_\alpha Q_{\alpha\beta}P_\beta)^2 \leq 2(P_\alpha P_\alpha)^2 \mathrm{Tr}\mathbf{Q}^2 \ ,$$

$$9(P_\alpha Q_{\alpha\beta}^2 P_\beta - \tfrac{1}{3}\mathrm{Tr}\mathbf{Q}^2 P_\alpha P_\alpha)^2 \leq (P_\alpha P_\alpha)^2 (\mathrm{Tr}\mathbf{Q}^2)^2 \ , \tag{13}$$

$$30(P_\alpha P_\beta P_\gamma \varepsilon_{\alpha\mu\nu} Q_{\mu\beta} O_{\nu\gamma})^2$$
$$\leq (P_\alpha P_\alpha)^3 [(\mathrm{Tr}\mathbf{Q}^2)^3 - 6(\mathrm{Tr}\mathbf{Q}^3)^2] \ .$$

The inequalities (13) are useful for the stability analysis of any expansion in terms of $\mathbf{P}$ and $\mathbf{Q}$.
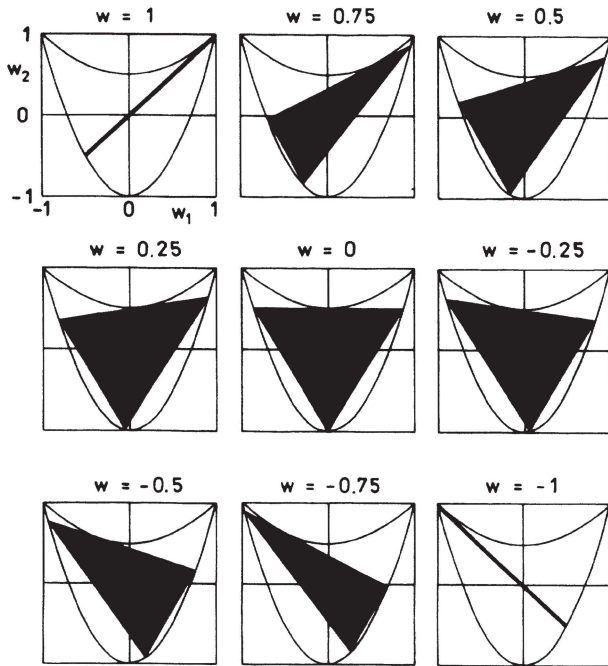

FIG. 2. Allowed variation of the independent degrees of freedom w_1 and w_2 for fixed w. The accessible states belong to the triangle inscribed into the area between two parabolas, Eqs. (12).
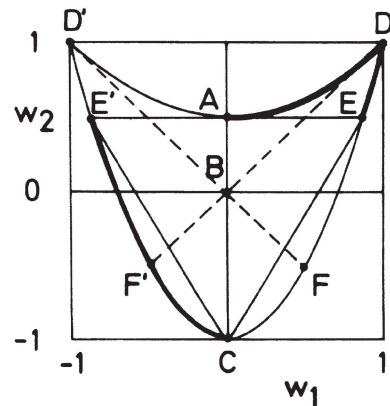

FIG. 3. Accessible states (w, w_1, w_2) projected onto the (w_1, w_2) plane. The identification of various points and arcs is given in Table I. The continuous, bold line represents prolate states.

IV. APPLICATIONS

We now apply the results of Sec. III to identify all polar states that follow from the minimization of an arbitrary invariant free-energy polynomial in the components of $Q_m^{(2)}$ and $P_m^{(1)}$. It is shown how the broken symmetry states are selected by properties of the integrity basis. We also develop a general theory of flexoelectricity and discuss the role played by integrity-basis elements in the formation of chiral biaxial phases, in particular of Sm-C^* phase.

The analysis of Secs. IV A and IV B is restricted to the case where only bulk invariants of P and Q are considered. Some aspects of the theory which includes elastic deformations of the order parameters are given in Secs. IV C and IV D (see also Ref. 20).

A. Local polar structures of chiral biaxial liquid crystals: interpretation of integrity-basis invariants

We start our analysis by locating all different prolate nematic $(w \geq 0)$ and ferroelectric states in the admitted range (Figs. 2 and 3). Corresponding statements are obtained for oblate states by applying the symmetry operation $(w, w_1) \leftrightarrow (-w, -w_1)$.

The prolate nematic, ferroelectric states are divided into two groups according to the equilibrium value of the invariant I_{33}. As upon the application of the inversion operation, this invariant changes sign; the states with P and $-P$ have different free energy. Therefore, we denote equilibrium states with $I_{33} \neq 0$ as chiral biaxial piezoelectric. The cosine w_3 is a measure of biaxial piezopolarization.

1. Ferroelectric states with $I_{33} = 0$

All states (i.e., values of Q and P or Q, P, w_α) with $I_{33} = 0$ belong to the surface $\partial \Omega$ of Ω. We can distinguish three groups (see Table I).

(i) A uniaxial, polar nematic state (F_{U1}), corresponding to points $\{D, F'\}$ of Fig. 3. The polarization is parallel to the local director.

(ii) A biaxial nematic state $(F_{B\parallel})$ with polarization parallel to one of the main tensor directions. All states with this property are located on arcs DE and CE' of parabola $D'CD$, Fig. 3, with exclusion of points $\{D, F'\}$.

(iii) A biaxial, polar nematic state (F_{Bg}) with polarization in a plane spanned by two eigenvectors of $Q_{\alpha\beta}$. These states cover the whole part of the surface $\partial \Omega$ for

TABLE I. Identification of polar states generated by the integrity basis, Eqs. (10). The arrowless lines represent nondegenerate main directions of the tensor Q. The arrows represent the orientation of the polarization vector P with respect to the main directions of Q. Note that prolate states correspond to the case of $w > 0$. Corresponding oblate states are obtained from prolate ones by applying the transformation which changes (w, w_1) onto $(-w, -w_1)$.

Phase	Values of angle variables	Localization of state in Fig. 3	Graphical representation of state
F_{U1}	$w = w_1 = \pm 1,$ $w_2 = 1, \ w_3 = 0$	Points $\{D, D'\}$	
	$w = \pm 1, \ w_3 = 0$ $w_1 = \pm w_2 = \mp \frac{1}{2}$	Points $\{F, F'\}$	
F_{U2}	$w = 1, \ w_1 = w_2,$ $w_3 = 0, \ -\frac{1}{2} < w_1 < 1$	Interval (F', D)	
	$w = -1, \ w_1 = -w_2,$ $w_3 = 0, \ -1 < w_1 < \frac{1}{2}$	Interval (FD')	Degenerate F_{Bg} phase
$F_{B\parallel}$	$(w, w_1, w_2) = (4w_1^3 - 3w_1, w_1, 2w_1^2 - 1),$ $-1 < w_1 < w, \ w_3 = 0$	Parabola $(D'CD)$ with exclusion of points $\{D, D', F, F'\}$	
F_{Bg}	$w_2 = Aw_1 + (1 - A^2)/2,$ $w = A(3 - A^2)/2,$ $|A| < 2, \ w_3 = 0,$ where (w_1, w_2) do not belong to parabola (D', CD)	Interior of area restricted by parabolas $(D'AD)$ and $(D'CD)$	
F_{ch}	Interior of volume $\Omega; \ w_3$ is determined from Eq. (10e)	Interior of area restricted by parabolas $(D'AD)$ and $(D'CD)$	

which $w \geq 0$ except the points of parabola $D'CD$. For the open interval $(F'D)$, the F_{Bg} state degenerates to a uniaxial state, F_{U2}, with polarization vector on a cone centered around the director. In this case only the component of **P** parallel to the director is contributing to a macroscopic polarization.

2. Chiral piezoelectric biaxial states with $I_{33} \neq 0$

These states carry angle variable in the interior $\Omega \setminus \partial\Omega$ of the volume Ω, where the invariant I_{33} is nonzero, and yield what we call the F_{ch} phase. The polarization in the F_{ch} phase cannot be parallel to a plane spanned by the eigenvectors of $Q_{\alpha\beta}$, and thus this phase must necessarily be *biaxial* [otherwise, as follows from Eq. (10b), the invariant I_{33} is zero].

For a fixed value of w, the piezopolarization of the F_{ch} state increases from the surface $\partial\Omega$ towards the point $w = w_1 = w_2 = 0$ (point B in Fig. 3). Maximal piezopolarization $(w_3^2)_{\max} = \frac{5}{9}$ is approached for $w_1 = w_2 = 0$ and $|w| \neq 1$ (point B in Fig. 3), where the polarization is parallel to one of the directions $\pm\hat{m}\pm\hat{n}\times\hat{m}\pm\hat{n}$. States of identical piezopolarization form a closed loop around the direction of maximal piezopolarization. As the free energy for the F_{ch} state is not inversion invariant, it must be supplemented by gradient terms. Consequently, $\underline{Q}$ and **P** ought to be position dependent. This is the reason why we denote the states discussed here as "local."

The invariant I_{33}, which is interpreted as "chiral strain," may be caused by biaxial molecules or by induced biaxialities and by chiral interactions. It is expected to be relevant for "truly" biaxial chiral mesogenic molecules.

B. Minimization of the bulk free energy: simple example

As demonstrated in Sec. IV A the analysis of the integrity basis leads to a qualitative understanding of the polar states that may appear in biaxial liquid crystals. Moreover, it applies to any SO(3) symmetric free energy expanded in terms of $Q_{\alpha\beta}$ and an arbitrary polar field, which, for example, could also be an electric (**E**) or magnetic (**H**) field or a gradient of the mass density $(\partial_\mu \rho)$. In the former case one arrives at the Landau theory of the nematic-isotropic phase transition in the presence of an external field while the latter case describes smectic-A and smectic-C phases (see Sec. IV D). Always the objective is to minimize a free energy with respect to P_α and $Q_{\alpha\beta}$. The process of minimization considerably simplifies if the variables P, Q, w, and w_α ($\alpha = 1, 2, 3$) are used.

From Sec. III we know that an arbitrary free-energy expansion analytical in the components P_α and $Q_{\alpha\beta}$ is a polynomial in the integrity-basis elements $I_{\alpha\beta}$ and linear function in I_{33}. Higher powers of I_{33} are eliminated by relation (10d). The analysis must take regard of the restrictions (12). Now, parametrizing the invariants (10) in terms of the set of variables

$$\Gamma = (Q \geq 0, P \geq 0, -1 \leq w \leq 1, -1 \leq w_\alpha \leq 1 , \quad \alpha = 1, 2, 3$$

we can minimize the free energy with respect to Γ only under constraints (10e) and (12). As an example let us

consider a nematic liquid crystal in an external, static magnetic field **H** of components H_α. The presence of the field leads to extra terms in the free-energy expansion (8), in lowest order to [see Eqs. (1)]

$$F_m = -\tfrac{1}{2}\Delta\chi_{\max}H_{\max}H_\alpha H_\beta Q_{\alpha\beta} , \qquad (14)$$

where $\Delta\chi_{\max}$ can be both positive and negative. Assuming that $\beta = -1$ and $\gamma = 1$ in (8), which is equivalent to fixing the scale for the free energy and for **Q**, the complete free energy is

$$F \equiv F(w, w_1)$$
$$= \alpha Q^2 - Q^3 w + Q^4 + \delta Q^5 w + \varepsilon Q^6 + \varepsilon' Q^6 w^2 - hQw_1 , \qquad (15)$$

with

$$h = (\sqrt{5}/6)^{1/2}\Delta\chi_{\max}H_\alpha H_\alpha .$$

Due to the absence of w_2 in the expansion (15), the minimum is approached on the parabola $D'CD$ of Fig. 3, so the problem reduces to finding minima of

$$F(w, w_1) = F(4w_1^3 - 3w_1, w_1) ,$$

where $|w_1| \leq 1$. For $h > 0$ and for small Q the fifth- and sixth-order terms are irrelevant and the minimum corresponds to $w = w_1 = 1$ (uniaxial prolate phase, point D in Fig. 3). With increasing value of Q the term quadratic in w (weighted by ε') is responsible for the approach of another, deeper minimum for $w < 1$, corresponding to the states located on the arc DE of the parabola $D'CD$. Since $w < 1$, these states are biaxial, prolate phases with the field parallel to the director (see Table I) and cover all the cases known for liquid crystals with positive diamagnetic susceptibility.

For negative $\Delta\chi_{\max}$ ($h < 0$) and for small Q the minimum is taken by the states represented by the point D' in Fig. 3 ($w_1 = -1$) which is an oblate, field-induced uniaxial nematic phase. With decreasing temperature (lowering α), another minimum appears covering arc DF'. The resulting structure is an oblate or prolate biaxial phase.

Addition of higher-order terms in w_1 to the free-energy expansion (15) does not change the results. The minima still are localized on the parabola $(D'CD)$. Thus, we can conclude that the coupling term, Eq. (14) (or, equivalently, I_{21}), is responsible for structures in which polarization (or any other vector property) is parallel to one of the tensor main axes. A similar analysis with the I_{22} invariant shows that the preferred structure is the one described as F_{Bg}. The presence of the I_{33} invariant generates a phase with the F_{ch} structure at low temperatures.

C. Generalized theory of flexopolarization in biaxial liquid crystals

In this section and in Sec. IV D some implications of a spatial dependence of **Q** and its consequences for form of the polarization field are discussed. We restrict ourselves to flexopolarization induced by a curvature of the molec-

ular orientation pattern and again apply the concept of integrity bases to construct systematically a general flexopolarization part of the free energy for biaxial systems.

As shown by Meyer,[7] flexopolarization originates from the coupling between splay or bend deformations and the shape of the molecules. Alternatively, a polarization requires a preferred orientation of the asymmetric molecules, which induces splay or bend curvature. Another possibility is that the polarization couples to the gradient of the scalar order parameter, S[9,20], as happens at the solid-liquid interface or in the vicinity of defects.

Both cases can be generalized to biaxial liquid crystals by assuming that the deformation-induced polarization depends on $Q_{\alpha\beta}$ and its gradient $\partial_\alpha Q_{\beta\gamma}$ at each point. Since the effect is linear in the deformations, only terms linear in $\partial_\alpha Q_{\beta\gamma}$ are relevant. The corresponding expansion of the free energy must include the class of linearly independent SO(3)-symmetric invariants built up from the tensors

$$\mathbf{PQQ}\cdots\mathbf{Q}(\partial\mathbf{Q})\equiv P_\xi Q_{\alpha\beta}Q_{\gamma\delta}\cdots Q_{\rho\sigma}(Q_{\mu\nu,\eta})$$

by means of contractions with the Kronecker symbols and the Levi-Civita tensors.

The tensors $\mathbf{PQQ}\cdots\mathbf{Q}(\partial\mathbf{Q})$ are written in spherical tensor notation as

$$\mathbf{PQQ}\cdots\mathbf{Q}(\partial\mathbf{Q})\equiv\left[\mathbf{P}^{(1)}\otimes\left[\overset{n}{\underset{i=1}{\otimes}}\mathbf{Q}^{(2)}\right]^{(M)}\otimes\partial\mathbf{Q}^{(L)}\right]^{(0)},$$

(16a)

where

$$\partial\mathbf{Q}^{(L)}\equiv[\partial^{(1)}\otimes\mathbf{Q}^{(2)}]^{(L)},\quad L=1,2,3.$$

(16b)

Now, using the properties of the integrity basis (6) we can compose the tensors

$$\left[\overset{n}{\underset{i=1}{\otimes}}\mathbf{Q}^{(2)}\right]^{(M)}$$

from an infinite set of tensors of the form

$$(\mathbf{I}_{02})^m(\mathbf{I}_{03})^n\left[\left[\overset{n_1}{\underset{i=1}{\otimes}}\mathbf{I}_{0,1}^{(2)}\right]^{(2n_1)}\otimes\left[\overset{n_2}{\underset{j=1}{\otimes}}\mathbf{I}_{0,2}^{(2)}\right]^{(2n_2)}\right]^{(2n_1+2n_2)},$$

(16c)

$$(\mathbf{I}_{02})^m(\mathbf{I}_{02})^n\left[I_{0,3}^{(3)}\otimes\left[\left[\overset{n_1}{\underset{i=1}{\otimes}}\mathbf{I}_{0,1}^{(2)}\right]^{(2n_1)}\otimes\left[\overset{n_2}{\underset{j=1}{\otimes}}\mathbf{I}_{0,2}^{(2)}\right]^{(2n_2)}\right]^{(2n_1+2n_2)}\right]^{(2n_1+2n_2+3)},$$

(16d)

where m,n,n_1,n_2 run over the nonnegative integers and where

$$\left[\overset{n}{\underset{i=1}{\otimes}}\mathbf{A}^{(J)}\right]^{(nJ)}\equiv\left[\cdots\otimes\left[\mathbf{A}^{(J)}\otimes\left[\mathbf{A}^{(J)}\otimes\mathbf{A}^{(J)}\right]^{(2J)}\right]^{(3J)}\cdots\right]^{(nJ)}.$$

By substituting the results (16c) and (16d) into the relation (16a), one finds the following equivalent form of the invariants (16a):

$$(\mathbf{I}_{02})^{n_1}(\mathbf{I}_{03})^{n_2}\Pi_\alpha,\quad \alpha=1,2,3$$

(16e)

where Π_α are so-called irreducible invariants, i.e., they cannot be expressed as polynomials of invariants of lower order. We can identify the following 12 of them:

For $n=0$, Π_1,

$$[\mathbf{P}^{(1)}\otimes\partial\mathbf{Q}^{(1)}]^{(0)}.$$

For $n=1$, Π_2,Π_3,Π_4,

$$[\mathbf{P}^{(1)}\otimes[\mathbf{Q}^{(2)}\otimes\partial\mathbf{Q}^{(L)}]^{(1)}]^{(0)},\quad L=1,2,3.$$

For $n=2$, $\Pi_5,\ldots,\Pi_8$,

$$[\mathbf{P}^{(1)}\otimes[[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(2)}\otimes\partial\mathbf{Q}^{(L)}]^{(1)}]^{(0)},\quad L=1,2,3.$$

$$[\mathbf{P}^{(1)}\otimes[[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(4)}\otimes\partial\mathbf{Q}^{(3)}]^{(1)}]^{(0)}.$$

For $n=3$, Π_9,Π_{10},Π_{11},

$$[\mathbf{P}^{(1)}\otimes[[\mathbf{Q}^{(2)}\otimes[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(2)}]^{(3)}\otimes\partial\mathbf{Q}^{(L)}]^{(1)}]^{(0)},\quad L=2,3.$$

$$[\mathbf{P}^{(1)}\otimes[[\mathbf{Q}^{(2)}\otimes[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(2)}]^{(4)}\otimes\partial\mathbf{Q}^{(3)}]^{(1)}]^{(0)}.$$

For $n=4$, Π_{12},

$$[\mathbf{P}^{(1)}\otimes[[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(2)}\otimes[\mathbf{Q}^{(2)}\otimes\mathbf{Q}^{(2)}]^{(2)}]^{(4)}\otimes\partial\mathbf{Q}^{(3)}]^{(1)}]^{(0)}.$$

In summary, the general flexopolarization free-energy density of chiral biaxial liquid crystals is composed of 12 basic deformation modes expressed by the terms Π_α, $\alpha=1,\ldots,12$. Those can be multiplied by arbitrary polynomials in the invariants $\mathbf{I}_{02}$ and $\mathbf{I}_{03}$, which define temperature-dependent flexocoefficients.

Special cases of the flexoelectric free-energy density are obtained from the general expansion by imposing additional symmetry restrictions on the field $\mathbf{Q}$. We follow the scheme proposed in Ref. 16 and reduce the number of independent flexopolarization modes Π_α for "soft biaxial nematic phases" by requiring

$$\sqrt{5}\mathbf{I}_{02} = \mathrm{Tr}\mathbf{Q}^2 = \mathrm{const} \ ,$$

for biaxial nematic phases with

$$\left(\tfrac{12}{35}\right)^{1/2}\mathbf{I}_{03} = \mathrm{Tr}\mathbf{Q}^3 = \mathrm{const}$$

and for hard biaxial phases by requiring both.

Meyer's original free energy[7] for uniaxial nematic liquid crystals also is deduced from the general case by taking regard of the uniaxiality condition (1d)

$$10(\mathbf{I}_{02})^3 = 7\sqrt{5}(\mathbf{I}_{03})^2 \ . \tag{17a}$$

With the conditions for the hard biaxial phase added, Eq. (17a) further decreases the number of irreducible invariants. The particular representation of Meyer in terms of the director $\hat{\mathbf{n}}$ is obtained if $\mathbf{Q}$ is expressed as in Eq. (1c) with $b = 0$.

From the symmetry requirements mentioned above, relations between the derivatives of $\mathbf{Q}$ are deduced by forming the derivatives of the position-independent integrity-basis elements $\mathbf{I}_{02}$ and $\mathbf{I}_{03}$ and equating them to zero:[16]

$$\partial_m^{(1)}\mathbf{I}_{0A} = \frac{\sqrt{3}}{\sqrt{5}}\sum_{J=1}^{3}\sqrt{2J+1}[\mathbf{I}_{0,A-1}^{(2)}\otimes\partial\mathbf{Q}^{(J)}]_m^{(1)} = 0 \quad \forall m \ , \tag{17b}$$

where $A = 2,3$. The vector equations (17b) are equivalent to the set of scalar equations

$$\left[\mathbf{P}^{(1)}\otimes\left[\left[\overset{n}{\underset{i=1}{\otimes}}\mathbf{Q}^{(2)}\right]^{(M)}\otimes\partial^{(1)}\mathbf{I}_{0A}\right]^{(1)}\right]^{(0)} = 0 \ , \tag{17c}$$

where

$$\left[\overset{n}{\underset{i=1}{\otimes}}\mathbf{Q}^{(2)}\right]^{(M)}$$

is given by Eqs. (16c) and (16d). Equations (17) lead to three independent relations between Π invariants for each allowed value of A. They read as follows:

(i) For $\mathrm{Tr}\mathbf{Q}^2 = \mathrm{const}$

$$\sqrt{3}\Pi_2 + \sqrt{5}\Pi_3 + \sqrt{7}\Pi_4 = 0 \ , \tag{18a}$$

$$2\sqrt{3}\sqrt{5}\mathbf{I}_{02}\Pi_1 + \sqrt{3}\sqrt{5}\sqrt{7}\Pi_5 - 5\sqrt{7}\Pi_6 + 2\sqrt{5}\Pi_7$$
$$+ 6\sqrt{3}\sqrt{5}\Pi_8 = 0 \ , \tag{18b}$$

$$7\sqrt{3}\sqrt{5}\mathbf{I}_{03}\Pi_1 + 5\sqrt{3}\sqrt{7}\mathbf{I}_{02}\Pi_2 - 5\sqrt{5}\sqrt{7}\mathbf{I}_{02}\Pi_3 + 10\mathbf{I}_{02}\Pi_4$$
$$- 7\sqrt{2}\sqrt{5}\sqrt{7}\Pi_9 + 7\sqrt{5}\sqrt{7}\Pi_{10} + 21\sqrt{3}\sqrt{5}\Pi_{11} = 0 \ . \tag{18c}$$

(ii) For $\mathrm{Tr}\mathbf{Q}^3 = \mathrm{const}$

$$\sqrt{3}\Pi_5 + \sqrt{5}\Pi_6 + \sqrt{7}\Pi_7 = 0 \ , \tag{18d}$$

$$7\sqrt{3}\sqrt{5}\mathbf{I}_{03}\Pi_1 + 5\sqrt{3}\sqrt{7}\mathbf{I}_{02}\Pi_2 - 5\sqrt{5}\sqrt{7}\mathbf{I}_{02}\Pi_3 + 10\mathbf{I}_{02}\Pi_4$$
$$+ 7\sqrt{2}\sqrt{5}\sqrt{7}\Pi_9 - 7\sqrt{5}\sqrt{7}\Pi_{10} + 21\sqrt{3}\sqrt{5}\Pi_{11} = 0 \ , \tag{18e}$$

$$10\sqrt{3}\mathbf{I}_{02}^2\Pi_1 + 10\sqrt{3}\sqrt{7}\mathbf{I}_{03}\Pi_2 - 10\sqrt{5}\sqrt{7}\mathbf{I}_{03}\Pi_3$$
$$+ 20\mathbf{I}_{03}\Pi_4 - 5\sqrt{3}\sqrt{7}\mathbf{I}_{02}\Pi_5 + 5\sqrt{5}\sqrt{7}\mathbf{I}_{02}\Pi_6$$
$$- 10\mathbf{I}_{02}\Pi_7 + 21\sqrt{3}\sqrt{5}\Pi_{12} = 0 \ . \tag{18f}$$

A situation qualitatively different from above is obtained if we require the phase to be uniaxial. Now, due to the restriction (17a), which is equivalent to the conditions (7c) and (7d), the number of analytically independent elements of the integrity basis for the field $\mathbf{Q}$ is reduced to $\mathbf{I}_2$ and $\mathbf{I}_2^{(2)}$ providing very simple relations between the irreducible invariants Π_α,

$$\Pi_{\alpha+3} = \Lambda\Pi_\alpha, \quad \alpha = 2,3,4$$
$$\Pi_9 = \Pi_{10} = 0 \ , \tag{19a}$$
$$\Pi_{12} = \Lambda\Pi_{11} = \Lambda^2\Pi_8 \ ,$$

where $\Lambda = \mathbf{I}_3/\mathbf{I}_2$. After that enormous reduction, we are left with five Π invariants:

$$\Pi_1,\ldots,\Pi_4,\Pi_8 \ . \tag{19b}$$

Still, not all of them are independent. An additional relation comes from the fact that the most general uniaxial field $\mathbf{Q}^{(2)}$ is representable as

$$\mathbf{Q}^{(2)} = [\mathbf{V}^{(1)}\otimes\mathbf{V}^{(1)}]^{(2)} \ , \tag{20a}$$

where $\mathbf{V}^{(1)}$ is an arbitrary vector field. Thus Π invariants of a general, uniaxial phase may be decomposed in the integrity basis of the invariants of a vector field, which yields one extra relation

$$84\sqrt{5}\mathbf{V}_{02}^2\Pi_1 - 210\mathbf{V}_{02}\Pi_2 + 70\sqrt{3}\sqrt{5}\mathbf{V}_{02}\Pi_3$$
$$- 20\sqrt{3}\sqrt{7}\mathbf{V}_{02}\Pi_4 + 105\Pi_8 = 0 \ , \tag{20b}$$

where

$$\mathbf{V}_{02} = [\mathbf{V}^{(1)}\otimes\mathbf{V}^{(1)}]^{(0)}$$

and

$$\mathbf{I}_{02} = \frac{2\sqrt{5}}{5}\mathbf{V}_{02}^2 \ .$$

The relation (20b) eliminates the Π_8 invariant. Thus the complete description of a general, uniaxial phase requires only four Π invariants.

Meyer's free energy is reproduced by assuming additionally that

$$[\mathbf{V}^{(1)}\otimes\mathbf{V}^{(1)}]^{(0)} = \mathrm{const} \ ,$$

which yields two more relations between the four independent invariants $\Pi_1,\ldots,\Pi_4$, obtained by combining Eqs. (18), (19a), and (20b). Finally, we are left with only two independent invariants Π_1 and Π_2 for a hard uniaxial phase. The whole reduction scheme is displayed in Fig. 4, where, as a rule, the invariants with lowest possible indices are retained.

Though the spherical representation readily helps to solve the problem of number and form of flexoelectric invariants, in many calculations it is more convenient to use the Cartesian representation, as the calculations of

General Biaxial Phase
$\Pi_1, \ldots, \Pi_{12}$

Soft Biaxial Phase
$Tr\mathbf{Q}^2 = const$
$\Pi_1, \ldots, \Pi_3, \Pi_5, \ldots, \Pi_7, \Pi_9, \Pi_{10}, \Pi_{12}$

General Uniaxial Phase
$(Tr\mathbf{Q}^2)^3 = 6(Tr\mathbf{Q}^3)^2$
$\Pi_1, \ldots, \Pi_4$

Biaxial Phase of $Tr\mathbf{Q}^3 = const$
$\Pi_1, \ldots, \Pi_6, \Pi_8, \ldots, \Pi_{10}$

Hard Biaxial Phase
$\Pi_1, \Pi_2, \Pi_3, \Pi_5, \Pi_6, \Pi_9$

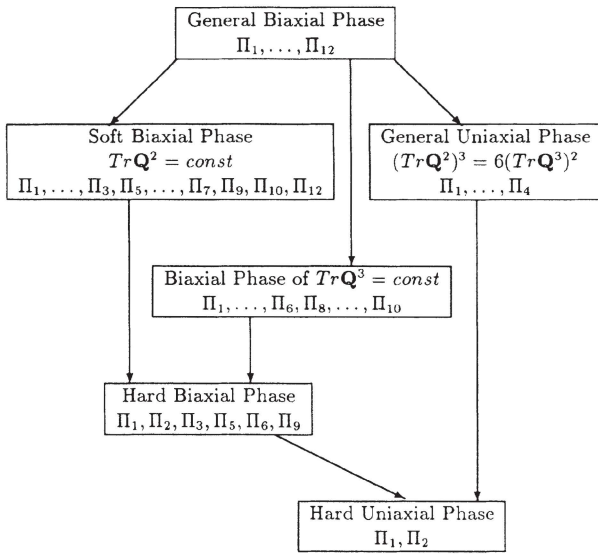Hard Uniaxial Phase
Π_1, Π_2

FIG. 4. The independent flexopolarization modes in various nematic phases as derived from the general biaxial case by special restrictions. Indicated are the independent irreducible Π invariants involved in the construction of the elastic free-energy density for each phase. As a rule, only terms with the lowest possible indices are retained.

Clebsch-Gordan coefficients are avoided and the free energy is written in a most compact form. In the present case the Cartesian form follows immediately from the relation $L = m$ between the momentum L of a spherical product and the number of independent Cartesian indices m of the Cartesian product. For example, this correspondence yields

$$\Pi_1 \equiv P_\alpha \partial_\beta Q_{\alpha\beta} \tag{21a}$$

$$\Pi_2 \equiv P_\alpha Q_{\alpha\beta} \partial_\mu Q_{\mu\beta} , \tag{21b}$$

or

$$\Pi_{12} \equiv P_\alpha [Q_{\alpha\gamma} Q_{\gamma\delta}][Q_{\mu\nu} Q_{\nu\rho}] \partial_\mu Q_{\delta\rho} . \tag{21c}$$

D. Chiral phases with simple helical structure

In this section the structural properties of simple chiral phases are investigated with the method of integrity bases because, as in the case of the Sm-C^* phases, chiral phases may be polar. Due to long-range deformations they must also be, at least weakly, biaxial, as has been demonstrated for cholesteric liquid crystals and blue phases by Grebel et al.[21] and will be shown to hold also for the smectic-C^* phase.

To determine possible equilibrium structures of chiral biaxial liquid crystals, we must minimize a free energy, which is the volume integral of the bulk free-energy density, composed of the integrity-basis elements (10), and of the elastic free-energy density involving gradients of $\mathbf{P}$ and $\mathbf{Q}$. In smectic liquid crystals, additionally, a density modulation must be taken into account, which is introduced by derivatives of the mass-density function, $\rho(\mathbf{r})$.

For a weak one-dimensional modulation as observed in smectic-A, -C, and -C^*, this mass density is expanded as

$$\rho(\mathbf{r}) = \rho_0 + 2\tau \exp[i(\mathbf{q}\cdot\mathbf{r} + \psi)] + \text{c.c.} , \tag{22a}$$

where τ is an amplitude, ψ an arbitrary phase, and $\mathbf{q}$ the wave vector. A measure of the modulation is given by the derivative

$$\partial_\mu \rho(\mathbf{r}) = 2i\tau q_\mu \exp[i(\mathbf{q}\cdot\mathbf{r} + \psi)] + \text{c.c.}$$

Since the free-energy expansion must be independent on ψ, the lowest-order energy terms are proportional to a uniaxial tensor,

$$T_{\mu\nu} = [\partial_\mu\rho(\mathbf{r})][\partial_\nu\rho(\mathbf{r})]^* \propto \tau^2 q_\mu q_\nu + \cdots \tag{22b}$$

where in case of modulation along the z axis $T_{\mu\nu} = T_{zz}\delta_{\mu z}\delta_{\nu z}$ (for comparison see Refs. 22 and 23).

Note that for the field $\mathbf{T}$ only two algebraically independent cross-coupling invariants exists with $\mathbf{Q}$, namely, $\text{Tr}(\mathbf{T}\mathbf{Q})$ and $\text{Tr}(\mathbf{T}\mathbf{Q}\mathbf{Q})$. As seen by inspection of Table I and Eqs. (10), the first invariant is responsible for smectic-A ordering, while the second one may give rise to smectic-C ordering. These terms, however, do not describe the polar structure of the smectic-C^* (Sm-C^*) phase, for which we need at least one piezoelectric chiral coupling term between $T_{\alpha\beta}$, $Q_{\mu\nu}$, and P_γ. The lowest-order coupling term of piezoelectric properties has the form

$$\varepsilon_{\alpha\mu\nu} T_{\alpha\beta} Q_{\mu\beta} P_\nu \tag{23}$$

and its minimum selects the symmetry of the Sm-C^* phase. For purely uniaxial deformations a similar term has been proposed in Ref. 23. Since the polarization in the Sm-C^* phase is perpendicular to the local director, the biaxial piezoelectric coupling invariant I_{33} must also vanish (see Table I).

An SO(3)-symmetric Landau-Ginzburg free energy of the Sm-C^* phase and of all higher-temperature phases is now formulated in a standard way as an expansion in $\mathbf{Q}$, $\mathbf{P}$, $\partial\mathbf{Q}$, and $\mathbf{T}$. In particular, the average quadratic part of the free-energy density is given by

$$F_2 = V^{-1} \int d\mathbf{r}[A \, Tr\mathbf{Q}^2 + L_1(\partial_\alpha Q_{\beta\gamma})(\partial_\alpha Q_{\beta\gamma})$$
$$+ L_2(\partial_\alpha Q_{\alpha\gamma})(\partial_\beta Q_{\beta\gamma}) - 2d\varepsilon_{\alpha\beta\gamma}Q_{\alpha\delta}\partial_\beta Q_{\gamma\delta}$$
$$- a_1 P_\alpha \partial_\beta Q_{\alpha\beta} + a_2 \mathbf{P}^2] , \tag{24}$$

where, as usual A is proportional to a reduced temperature $[A = a(T - T^*), \ a > 0]$ and a_2, L_1, L_2, d, and a_4 are regarded as temperature-independent coefficients. Since dipolar interactions in liquid crystals have antiferroelectric character, the parameter a_2 is positive. The gradient terms weighted by the elastic constants L_1, L_2 describe the elastic free energy.[3] The term proportional to d disappears in the absence of chiral interactions. This term is, for example, responsible for the helicoidal structure of cholesteric liquid crystals and blue phases. For stability of the helix of the smectic-C^* phase we additionally need at least one piezoelectric term of the form (23). The term weighted by a_1 is the lowest-order flexopolarization invariant.

Five linearly independent invariants containing $\mathbf{T}$ or $\partial_\alpha P_\beta$ and $\partial_\alpha Q_{\beta\gamma}$ (Ref. 20) are disregarded since they either do not influence the spatial dependence of $\mathbf{Q}$ or are negligible in the limit of weak antiferroelectric interactions. Note also that a possible coupling term $Q_{\alpha\beta}\partial_\alpha P_\beta$ is equivalent (up to a full divergence) to the flexopolarization coupling term already included in the expansion (24).

In the free-energy expansion, gradient and bulk invariants usually favor different structures and make the identification of equilibrium structures extremely difficult. Therefore we restrict our analysis to phases with simple helicoidal structure.

We first introduce a parametrization of the order parameters that agrees with the symmetries of the observed phases by expanding $\mathbf{Q}$ and $\mathbf{P}$ into plane waves of helicity

$$\mathbf{Q}(\mathbf{r})=\sum_{*\mathbf{k}}\frac{1}{(N_{*\mathbf{k}})^{1/2}}\left[\sum_{\mathbf{k}\in *\mathbf{k}}\mathbf{Q}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r})\right] , \qquad (25a)$$

where

$$\mathbf{Q}(\mathbf{k})=\left\{\sum_{m=-2}^{2}Q_{m,\mathbf{k}}^{[2]*}(\mathbf{k})\mathbf{e}_{m,\mathbf{k}}^{[2]}\right\} \qquad (25b)$$

and where

$$Q_{m,\mathbf{k}}^{[2]}(\mathbf{k})=|Q_{m,\mathbf{k}}^{[2]}(\mathbf{k})|\exp(i\psi_{m,\hat{\mathbf{k}}}) . \qquad (25c)$$

Here $\mathbf{k}$ is taken out of a reciprocal lattice of a space group $\mathbb{G}$, where

$$*\mathbf{k}=\{\mathbf{k}':\mathbf{k}'=S\mathbf{k}, \{S|t\}\in\mathbb{G}\}$$

is the star of $\mathbf{k}$, $N_{*\mathbf{k}}$ is the number of prongs of the star $*\mathbf{k}$,

$$|Q_{m,\mathbf{k}}^{[2]*}(\mathbf{k})|=Q_m(|\mathbf{k}|)=Q_m(k)\geq 0$$

are variational parameters in the expansion, and, finally,

$$\mathbf{e}_{0,\mathbf{k}}^{[2]}=\frac{1}{\sqrt{6}}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} ,$$

$$\mathbf{e}_{\pm1,\hat{\mathbf{k}}}^{[2]}=\tfrac{1}{2}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & \pm i \\ 1 & \pm i & 0 \end{bmatrix} ,$$

$$\mathbf{e}_{\pm2,\hat{\mathbf{k}}}^{[2]}=\tfrac{1}{2}\begin{bmatrix} 1 & \pm i & 0 \\ \pm i & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

are spin $L=2$ tensors represented in an orthogonal, right-handed local coordinate system with $\hat{\mathbf{k}}$ as quantization axis. The selection of wave vectors $\mathbf{k}$ and phases $\psi_{m,\hat{\mathbf{k}}}$ fixes the symmetry of the phase.

For the polarization field we write similarly

$$\mathbf{P}(\mathbf{r})=\sum_{*\mathbf{k}}\frac{1}{(N_{*\mathbf{k}})^{1/2}}\left[\sum_{\mathbf{k}\in *\mathbf{k}}\mathbf{P}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r})\right] , \qquad (26a)$$

where

$$\mathbf{P}(\mathbf{k})=\left\{\sum_{m=-2}^{2}\mathbf{P}_{m,\mathbf{k}}^{[1]*}(\mathbf{k})\mathbf{e}_{m,\mathbf{k}}^{[1]}\right\} \qquad (26b)$$

and

$$\mathbf{P}_{m,\mathbf{k}}^{[1]}(\mathbf{k})=|\mathbf{P}_{m,\mathbf{k}}^{[1]}(\mathbf{k})|\exp(i\phi_{m,\hat{\mathbf{k}}})=P_m(k)\exp(i\phi_{m,\hat{\mathbf{k}}}) . \qquad (26c)$$

Here $\mathbf{e}_{m,\mathbf{k}}^{[1]}$ are the spherical basis vectors

$$\mathbf{e}_{0,\mathbf{k}}^{[1]}=\hat{\mathbf{k}}=(0,0,1) ,$$

$$\mathbf{e}_{\pm1,\hat{\mathbf{k}}}^{[1]}=\frac{1}{\sqrt{2}}(1,\pm i,0) .$$

For chiral nematic liquid crystals (without external field) essentially two types of wave vector sets have been used in the past:

(a) A single wave vector (or set of parallel vectors). The corresponding order-parameter field is the biaxial spiral. This field describes exactly the cholesteric[21] phase and the Sm-C^* phase.

(b) Wave vectors out of a cubic reciprocal lattice. These enter the description of the cubic blue phases.[21]

As usual, the dominant contributions to the order-parameter expansion in various phases are found by studying the excitation spectrum of the quadratic part of the free energy, Eq. (24), which for the expansions (25) and (26) it is straightforward to evaluate

$$F_2=\sum_{\sigma,m}F_2(m,\sigma)=\sum_{\sigma,m}[F_{QQ}(m,\sigma)Q_m^2(\sigma)$$
$$+2F_{QP}(m,\sigma)Q_m(\sigma)P_m(\sigma)$$
$$+F_{PP}(m,\sigma)P_m^2(\sigma)] , \qquad (27a)$$

where

$$F_{QQ}(m,\sigma)=A-md\sqrt{\sigma}+\left[L_1+\frac{L_2}{6}(4-m^2)\right]k^2\sigma ,$$

$$F_{QP}(m,k)=-a_1k\sqrt{\sigma}\left[\frac{4-m^2}{6}\right]^{1/2} , \qquad (27b)$$

$$F_{PP}(m,k)=a_2\left[\frac{m-m^2+2}{2}\right] ,$$

and where σ is the sum of squares of Miller indices.

For thermodynamic stability of the isotropic phase ($\mathbf{Q}=\underline{0}$, $\mathbf{P}=0$) at high temperatures we must require, in addition to $a_2>0$, that

$$L_1>0 \quad\text{and}\quad L_1+\tfrac{2}{3}\left[L_2-\frac{a_1^2}{a_2}\right]>0 . \qquad (27c)$$

The excitation spectrum that follows from F_2 is given by the eigenvalues of the matrix $\hat{\mathbf{F}}$,

$$\hat{\mathbf{F}}=\begin{bmatrix} F_{QQ} & F_{QP} \\ F_{QP} & F_{PP} \end{bmatrix} .$$

The various branches of the spectrum are labeled by the quantum numbers m and σ. Each branch of the spec-

trum has its own minimum as a function of k. For positive chirality $(d \geq 0)$ these minima are taken at k vectors

$$[k \equiv k(\sigma, m), \quad m = -2, \ldots, 2]$$

fulfilling the conditions

$$k(2, \sigma) = k_2 = \frac{|d|}{L_1 \sqrt{\sigma}},$$

$$k(1, \sigma) = k_1 = \frac{|d|}{2\left[L_1 + \frac{1}{2}\left[L_2 - \frac{a_1^2}{a_2}\right]\right]\sqrt{\sigma}}, \quad (27d)$$

$$k(m, \sigma) = k_m = 0 \quad \text{for } m \leq 0 .$$

The corresponding maximal temperatures $T(m, \sigma) \equiv T_m$ $(m = 0, 1, 2)$ at which the successive branches $F_2(m, \sigma)$, Eq. (27a), with fixed m and d $(d \geq 0)$ become negative (unstable) are

$$T_2 = T^* + \frac{d^2}{aL_1},$$

$$T_1 = T^* + \frac{d^2}{4a\left[L_1 + \frac{1}{2}\left[L_2 - \frac{a_1^2}{a_2}\right]\right]}, \quad T_0 = T^* . \quad (27e)$$

The first instability towards an ordered state occurs at the temperature equal to the maximal one, T_m. For nonchiral systems (nematic, racemic, smectic-A, smectic-C, etc.), where $d = 0$, the instability is towards a phase with $k = 0$. For $d > 0$ the system is chiral and, due to the restriction (27c), the maximal temperature T_m is always equal to T_2. Thus, blue phases and cholesteric phase, both described by $m = 2$ modes,[21] are stabilized at higher temperatures than the Sm-C^* phase.[8]

For nonzero quadratic chiral terms, disregarded in the expansion (24), the temperature T_1 may become greater than T_2. In this case the ground-state tensor field contains $m = 1$ helix modes predominantly and, due to the associated tilt of the director, represents the Sm-C^* phase.

The ratio k_1/k_2 is, in principle, an arbitrary number. Therefore, incommensurate polar structures are also possible. Finally, if the helix mode $m = 0$ is present, then its amplitudes are strongest for $k = 0$. The same statements are valid for $d < 0$ if the sign of m is inverted.

With the results from the minimization of the quadratic part of the free energy, it is now straightforward to construct an approximate form of the alignment tensor $\mathbf{Q}$ and the polarization vector $\mathbf{P}$ for a simple helicoidal structures. Since our intention is to discuss the features of phase diagrams merely by the properties of the integrity basis, it is sufficient to consider a pair of vectors $(\mathbf{k}, -\mathbf{k})$ for each helicity m. Without loss of generality we can also restrict the values of m to $m \geq 0$. For cholesteric liquid crystals and Sm-C^* structures, where the modulation of $\mathbf{Q}$ is weak, both approximations introduced above are well justified.[21] Hence, the fields $\mathbf{Q}$ and $\mathbf{P}$ take the form

$$\underline{Q}_C(\mathbf{r}) = Q_0 \mathbf{e}_{0,\mathbf{k}}^{[2]} + \frac{1}{\sqrt{2}} Q_1 (e^{i(lkz + \psi_1)} \mathbf{e}_{1,\mathbf{k}}^{[2]} + \text{c.c.})$$

$$+ \frac{1}{\sqrt{2}} Q_2 [e^{i(mkz + \psi_2)} \mathbf{e}_{2,\mathbf{k}}^{[2]} + \text{c.c.}], \quad (28a)$$

$$\mathbf{P}_C(\mathbf{r}) = P_0 \mathbf{e}_{0,\mathbf{k}}^{[1]} + \frac{1}{\sqrt{2}} P_1 (e^{i(nkz + \phi_1)} \mathbf{e}_{1,\mathbf{k}}^{[1]} + \text{c.c.}], \quad (28b)$$

where c.c. stands for the complex conjugation, ψ_1, ψ_2, ϕ_1 for phases, and l, m, n for integers. One out of the three phases can be taken arbitrary which reflects a freedom of choosing the coordinate origin. Thus, two out of three phases ψ_1, ψ_2, ϕ_1, the amplitudes Q_0, Q_1, Q_2, P_0, P_1, and the integers l, m, n must be determined by the minimization of the full free energy.

The classical cholesteric phase is described by values $Q_0 \neq 0$, $Q_2 \neq 0$, $m = 1$, and $Q_1 = P_0 = P_1 = 0$, while the Sm-C^* phase corresponds to values $Q_0 \neq 0$, $Q_1 \neq 0$, $Q_2 \neq 0$, $P_1 \neq 0$, and $P_0 = 0$. Allowed values of l, m, n and of the phases ψ_1, ψ_2, ϕ_1 for Sm-C^* will be determined from a minimization of the piezoelectric coupling term. Since polarization in Sm-C^* phase is perpendicular to the director, this implies that, additionally, the $\mathbf{I}_{33}$ invariant must vanish.

The parametrization, Eq. (28), yields a biaxial tensor order parameter because $\text{Tr}\mathbf{Q}^2$ and $\text{Tr}\mathbf{Q}^3$ do not fulfill the uniaxiality condition (1d):

$$\text{Tr}\underline{Q}^2 = Q_0^2 + Q_1^2 + Q_2^2 \quad (29a)$$

and

$$\text{Tr}\underline{Q}^3 = \frac{\sqrt{2}}{12} \{9Q_1^2 Q_2 \cos[(2m - l)kz - \psi_2 + 2\psi_1]$$

$$+ \sqrt{3}(6Q_0 Q_2^2 - 3Q_0 Q_1^2 - 2Q_0^3)\} . \quad (29b)$$

The biaxiality parameter χ [Eq. (7g)] is position independent for $Q_1 = 0$ or $l = 2m$ and a periodic function otherwise. The periodic part of χ is due to Q_1 in the expansion (28a). Only for a particular choice of ratios Q_1/Q_0 and Q_2/Q_0—for example, $Q_1/Q_0 = 0$ and $Q_2/Q_0 = \pm\sqrt{3}$-does the parameter disappear. But this choice must not be met, because the values of these ratios are obtained by minimizing the full free energy (see, e.g., Ref. 21 for a discussion of biaxiality in the cholesteric phase).

In agreement with the discussion above the invariants, Eqs. (23) and (10b), determine the final form of the order parameters in the Sm-C^* phase. This is achieved by minimization of the piezoelectric invariant (23) and by the condition that the $\mathbf{I}_{33}$ invariant vanishes. By direct calculations of the invariants (23) and (10b) for the expansions (28), one arrives at

$$\epsilon_{\alpha\mu\nu} T_{\alpha\beta} Q_{\mu\beta} P_\nu = -\frac{P_1 Q_1 T_{zz} \sin[(n - m)z - \psi_1 + \phi_1]}{\sqrt{2}}$$

$$(30a)$$

and

$\epsilon_{\alpha\beta\gamma}P_\alpha P_\mu P_\nu Q_{\beta\mu}Q_{\gamma\rho}Q_{\rho\nu}$

$$
\begin{aligned}
=\frac{\sqrt{2}}{16}(P_1^3 Q_1 \{2Q_2^2 &\sin[(3n+m-2l)z-2\psi_2+\psi_1+3\phi_1]-2\sqrt{3}Q_0 Q_2 \sin[(3n-m-l)z-\psi_2-\psi_1+3\phi_1]\\
&-Q_1^2 \sin[3(n-m)z-3\psi_1+3\phi_1]\}+2\sqrt{3}P_0 P_1^2 Q_0 Q_1^2 \sin[2(n-m)z-2\psi_1+2\phi_1]\\
&+2P_0 P_1^2 Q_2(Q_1^2+6Q_0^2-2Q_2^2)\sin[(2n-l)z-\psi_2+2\phi_1]\\
&+2\sqrt{3}P_1(4P_0^2-P_1^2)Q_0 Q_1 Q_2 \sin[(n+m-l)z-\psi_2+\psi_1+\phi_1]\\
&+P_1 Q_1(4P_0^2-P_1^2)(Q_1^2-2Q_2^2)\sin[(n-m)z-\psi_1+\phi_1]\\
&+2P_0(2P_0^2-3P_1^2)Q_1^2 Q_2 \sin[(2m-l)z-\psi_2+2\psi_1]) ,
\end{aligned}
\tag{30b}
$$

which gives for the Sm-C^* structure,

$$
n=m=1, \quad l=2m ,
\tag{30c}
$$

$$
\phi_1-\psi_1=\frac{\pi}{2} \text{ or } \frac{3\pi}{2}, \quad \psi_2-2\psi_1=0 \text{ or } \pi, \text{ and } P_0=0 .
$$

Thus, the Sm-C^* phase is a uniform and biaxial spiral with two commensurate wave vectors k_1 and k_2, such that $k_l/k_2=l/m=2$. The last two features are not present in the standard director approach. The cubic invariant (10b) is also minimized by the parameters (30c). The other two elements of the integrity basis,

$$
P_\alpha Q_{\alpha\beta}P_\beta=\frac{\sqrt{2}}{6}\{3P_1^2 Q_2 \cos[(2n-l)z-\psi_2+2\phi_1]+6P_0 P_1 Q_1 \cos[(n-m)z-\psi_1+\phi_1]+\sqrt{3}P_1^2 Q_0-2\sqrt{3}P_0^2 Q_0\}
\tag{30d}
$$

and

$$
\begin{aligned}
P_\alpha Q_{\alpha\beta}Q_{\beta\gamma}P_\gamma=\frac{1}{12}\{3P_1^2 Q_1^2 &\cos[2(n-m)z-2\psi_1+2\phi_1]+12P_0 P_1 Q_1 Q_2 \cos[(n+m-l)z-\psi_2+\psi_1+\phi_1]\\
&+6P_1^2 Q_2^2+(3P_1^2+6P_0^2)Q_1^2+(2P_1^2+8P_0^2)Q_0^2\}+\frac{\sqrt{3}}{3}P_1 Q_0\{P_1 Q_2 \cos[(2n-l)z-\psi_2+2\phi_1]\\
&-P_0 Q_1 \cos[(n-m)z-\psi_1+\phi_1]\} ,
\end{aligned}
\tag{30e}
$$

are minimized for a Sm-C^* spiral provided that the signs of the coefficients weighting these terms in the Landau expansion are chosen correctly. Otherwise, a nonuniform spiral with position dependent η or incommensurate two- or three-dimensional structures may appear more stable. The latter can be selected by $\mathbf{I}_{21}$ and $\mathbf{I}_{22}$ invariants.

V. DISCUSSION

Many liquid crystalline phases are biaxial. These include the experimentally observed cholesteric phase, the blue phases, the smectic-C and -C^* phases, or the recently discovered thermotropic biaxial nematic liquid crystals.[24] Thus, a chemical synthesis of "truly" biaxial molecular fluids with chiral and possibly also polar centers does not seem to be remote. The symmetry of many mesogens is consistent with the requirements for a ferroelectric phase so that there is no fundamental reason for ferroelectric fluid phases not to exist. From this point of view it appears interesting to study systematically the properties of polar biaxial systems.

The description of such systems in terms of the standard director field is not general enough, and at least the traceless and symmetric quadrupole tensor order-parameter field must be introduced. In case of structures with polar order and density modulation (like smectic-C^* phases), a polarization field and gradients of local density of mass have to be added. With so many fields one is forced to study properties of these systems with an ap-

proach which, as far as possible, refers to the symmetry of the order parameters.

Here we have made an attempt at such an analysis using the concept of integrity bases. The proposed phenomenological free-energy expansion in terms of invariants of the order parameters is now complete up to all powers of the polarization field $\mathbf{P}$ and the alignment tensor $\mathbf{Q}$ and up to the terms linear in derivatives of $\mathbf{Q}$ (flexopolarization). The number, the explicit form, and the algebraic independence of the various invariants and their physical meaning follow directly from the properties of the integrity basis. Another advantage offered by the method of integrity bases is that of a very convenient parametrization of the free energy in terms of independent scalars, i.e., "lengths" of basic tensor order parameters and "angles" between them [see, e.g., Eqs. (10)].

If, as for nematic liquid crystals, the generating function for invariants only contains denominator terms, the "lengths" and the "angles" are independent variables and the minimization is straightforward. Restrictions of the range of values of the angles come from powers of numerator integrity-basis elements [compare, e.g., Eq.

(4a) with Eq. (9c)]. These may be taken into account when completing the free-energy expansion by appropriate Legendre multipliers. Thus, the problem of minimizing the Landau free energy simplifies considerably because usually the minimization with respect to an order parameter of nontrivial intrinsic symmetry is difficult for the spontaneously broken SO(3) symmetry[25] and for other continuous or discrete symmetries.

As an illustration we have discussed the properties of polar, biaxial liquid crystals. The classification of the resulting local, polar structures was directly inferred from the integrity-basis elements (10). Moreover, some qualitative predictions about phase diagrams were possible without numerical calculations: In polar biaxial systems only five different local polar structures, listed in Table I, can exist. They are linked with the cross-coupling invariants (10) between the alignment tensor Q and the polarization density P. In addition to the uniaxial and biaxial ferroelectric nematic states, the theory predicts a biaxial chiral ferroelectric nematic state, F_{ch}, which is selected by the I_{33} element, Eq. (10b), of the integrity basis, Eqs. (10). The F_{ch} state differs from others in that it cannot exist for a uniaxial phase. From the form of the I_{33} invariant one may speculate that the following conditions must be fulfilled for the existence of a phase of local F_{ch} symmetry: (i) chiral molecules with a large dipole moment component, perpendicular to the long molecular axis, and (ii) large molecular biaxiality, probably of the same order as the one observed in thermotropic biaxial nematics.[24]

Apart from a bulk polarization, a system may exhibit an induced polarization linked with local deformations of the tensor field. This flexopolarization effect was predicted by Meyer[7] for uniaxial nematic phases. Our attempt here was to extend the Meyer theory to the biaxial case. The most general SO(3)-invariant flexopolarization free-energy density was constructed up to all powers in the alignment tensor $Q_{\alpha\beta}$ and linear in the gradient $Q_{\alpha\beta,\gamma}$ and the polarization field P_α. The method provides all algebraically independent flexopolarization modes for nematic and cholesteric liquid crystals in the form of 12 fundamental invariants, Eqs. (18). These generalize the concept of splay- and bend-induced flexopolarizations introduced by Meyer.

To provide some insight into the meaning of various irreducible invariants, some symmetry restrictions of the field Q leading to a smaller number of the irreducible invariants were also discussed in detail. Following Ref. 16, we discussed the case of "soft" biaxial nematics phases by requiring $TrQ^2 = $const, a biaxial system with $TrQ^3 = $const, a biaxial system with fixed moduli of the order parameter ("hard biaxials") by requiring both, and two uniaxial cases (see Fig. 4). Hard uniaxials require only two irreducible invariants while "general uniaxials" double this number. Both limiting cases agree with those of Meyer[7] (hard uniaxials) and Barbero et al.[9] (general uniaxials). In the case of hard biaxials we obtained six irreducible invariants, i.e., two invariants more than found

by Pleiner et al. (Ref. 26, page 570). The most general case requires 12 irreducible invariants. These can additionally be multiplied by an arbitrary polynomial in I_{02} and I_{03}.

Finally, we discussed some structural properties of the ferroelectric smectic-C^* phase. Our intention was to generalize the standard director picture using a formalism of space group representations. A full description requires, apart from the alignment tensor Q and polarization P, inclusion of the density modulation. It leads, in the simplest approximation, to an additional tensor field T of rank 3 describing a one-dimensional density wave. The integrity basis for the invariants is found by applying formula (9b) recursively. Cross-coupling elements of the generalized integrity basis are responsible for polar, biaxial, and spatially modulated structures. Some of these invariants, relevant for smectic-A and smectic-C phases, have the same mathematical form as the I_{21} and I_{22} invariants, respectively. To describe the smectic-C^* phase one needs, apart from a flexoelectric coupling term, at least one extra piezoelectric term[23] which, in SO(3)-symmetric form, is given by Eq. (23).

A director description of the Sm-C^* phase is found in Refs. 23. These models must be generalized to describe properly cholesteric–smectic-C^* and isotropic–smectic-C^* phase transitions.[8] Due to the presence of deformations the Sm-C^* phase is at least weakly biaxial. In order to account for these effects, a full tensor field, polar field, and density wave are necessary. Then the smectic-C^* phase is described as a uniform polar biaxial spiral with two characteristic harmonics (one for each independent helicity mode) where the ratio of k vectors is 2 [see Eq. (30c)]. In agreement with experiment, polarity in this phase is restricted to the x-y plane provided that the smectic modulation is parallel to the z axis of a Cartesian coordinate system. This state is favored by the piezoelectric coupling (23) and makes I_{33} vanish. It also minimizes the cubic invariant I_{03} and the remaining invariants belonging to the integrity basis, provided that the signs of the weighting coefficients are properly chosen. Otherwise a nonuniform spiral or another state may appear more stable.

Other intriguing possibilities suggested by the quadratic part of the free energy are two- or three-dimensional incommensurate polar structures. These could, in principle, be generated by the integrity-basis elements I_{21} or I_{22}. A full account of this problem will be presented elsewhere. All algebraic calculations have been performed using algebraic processors MACSYMA and REDUCE.

ACKNOWLEDGMENTS

[1]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).

[2]*The Molecular Physics of Liquid Crystals,* edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979).

[3]P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971); see also P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1974).

[4]For a review see, e.g., (a) D. L. Johnson, J. Chim. Phys. **80**, 45 (1983); (b) T. C. Lubensky, J. Chim. Phys. **80**, 31 (1983); (c) E. F. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986).

[5](a) G. Siqaud, F. Hardouin, M. Achard, and H. Gasparoux, J. Phys. (Paris) Colloq. **3**, C-356 (1979); (b) A. M. Levelut, R. J. Tarento, F. Hardouin, M. Achard, and G. Siqaud, Phys. Rev. A **24**, 2180 (1981); (c) G. Siqaud, F. Hardouin, M. Achard, and A. M. Levelut, J. Phys. (Paris) **42**, 107 (1981); (d) G. Siqaud, M. Achard, and F. Hardouin, J. Phys. (Paris) Lett. **46**, L-825 (1985).

[6](a) P. E. Cladis, Phys. Rev. Lett. **35**, 48 (1978); (b) P. E. Cladis, D. Guillon, F. R. Bouchet, and P. L. Finn, Phys. Rev. A **23**, 2594 (1981); (c) G. Heppke, R. Hopf, B. Kohne, and K. Praefcke, *Advances in Liquid Crystal Research and Applications,* edited by L. Bata (Pergamon, Oxford, 1980); (d) F. Hardouin, Physica A **140**, 359 (1986).

[7]R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).

[8](a) R. B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, J. Phys. (Paris) Lett. L-69 (1975); (b) see, e.g., review by S. T. Lagerwall and I. Dahl, Mol. Cryst. Liq. Cryst. **114**, 151 (1984); (c) T. M. Leslie, Ferroelectrics **58**, 9 (1984); (d) J. L. Alabart, M. Marcos, E. Melendez, and J. L. Serrano, Ferroelectrics **58**, 37 (1984).

[9]G. Barbero, I. Dozov, J. F. Palierne, and G. Durand, Phys. Rev. Lett. **56**, 2056 (1986).

[10](a) A. Michelson, L. Benguigui, and D. Cabib, Phys. Rev. A **16**, 364 (1977); (b) R. Blinc, Ferroelectrics **16**, 33 (1977).

[11]A. G. Khachaturyan, J. Phys. Chem. Solids **36**, 1055 (1975).

[12]Invariants A, B, C, . . . are said to be algebraically independent if no polynomial relation $W(A,B,C,...)=0$ exists between them.

[13]T. Molien, Sber. Preuss. Akad. Wiss. **2**, 1152 (1897).

[14](a) B. R. Judd, W. Miller Jr., J. Patera, and P. Winternitz, J. Math. Phys. **15**, 1787 (1974); (b) R. Gaskell, A. Peccia, and R. T. Sharp, J. Math. Phys. **19**, 727 (1978); (c) J. Bystricky, J. Patera, and R. T. Sharp, J. Math Phys. **23**, 1560 (1982).

[15]H. -R. Trebin, L. Longa, and B. Salzgeber, Phys. Status Solidi B **144**, 73 (1987).

[16]L. Longa and H.-R. Trebin, Phys. Rev. A **39**, 2160 (1989).

[17]M. A. Lee, D. W. Allender, and S. Sharma (unpublished).

[18](a) K. Radley, L. W. Reeves, and A. S. Tracy, J. Phys. Chem. **80**, 174 (1976); (b) L. Y. Yu and A. Saupe, J. Am. Chem. Soc. **102**, 4879 (1980); (c) L. Y. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980); (d) A. Saupe, P. Boonbrahm, and L. J. Yu, J. Chim. Phys. **80**, 7 (1983).

[19](a) M. A. Anisimov, V. M. Mamnitskii, and E. L. Sorkin, J. Eng. Phys. (USSR) **39**, 1285 (1981); (b) M. A. Anisimov, V. M. Zaprudskii, V. M. Mamnitskii, and E. L. Sorkin, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 166 (1979) [JETP Lett. **30**, 491 (1979)]; (c) M. A. Anisimov, R. S. Garber, V. S. Esipov, V. M. Mamnitskii, J. I. Ovodov, L. A. Smolenko, and E. L. Sorkin, Zh. Eksp. Teor. Fiz. **72**, 1983 (1977) [Sov. Phys.—JETP **45**, 1042 (1977)].

[20]L. Longa, D. Monselesan, and H.-R. Trebin, Liquid Crystals **6**, 769 (1987).

[21]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983).

[22]E. E. Gorodecki and V. E. Podnek, Kristallografiya **29**, 1054 (1984).

[23](a) V. L. Indenbon, S. A. Pikin, and E. B. Loginov, Kristallografiya **21**, 1093 (1976); (b) S. A. Pikin, *Structural Transformations in Liquid Crystals* (Nauka, Moscow, 1981); (c) B. Žekš, Mol. Cryst. Liq. Cryst. **114**, 259 (1984); (d) T. Carlsson, B. Žekš, A. Levstik, C. Filipič, I. Levstik, and R. Blinc, Phys. Rev. A **36**, 1484 (1987).

[24](a) S. Chandrasekhar, B. K. Sadashiva, S. Ramasha, and B. S. Srikanta, J. Phys. (Paris) Lett. **27**, L713 (1986); (b) J. Malthete, L. Liebert, and A. M. Levelut, C. R. Acad. Sci. (Paris) **303**, 1073 (1986).

[25]M. V. Jaric, Nucl. Phys. B **265**, 647 (1986).

[26]H. R. Brandt and H. Pleiner, J. Phys. (Paris) **45**, 563 (1984).