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THEORY OF LIQUID CRYSTALLINE PHASES IN BIAXIAL SYSTEMS.

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Abstract **General properties of SO(3) - symmetric free- energy expansion for biaxial systems are studied. In particular, all invariants in powers of a traceless and symmetric quadrupole tensor order parameter and a vector order parameter are identified and their relation to possible local structures are found. A new class of polar, chiral biaxial phases are predicted.**

Keywords: biaxial systems; order parameters; invariant expansion; S_C** *phases*

INTRODUCTION

Many liquid crystalline phases are biaxial[1-4]. These include the experimentally observed cholesteric phase, the blue phases and the smectic C^* phase. In these phases biaxiality is weak and originates from the local deformations of the molecular orientations. The recently discovered thermotropic biaxial nematic phase[4] provides another example of a biaxial system. Here, unlike the previous case, the long range biaxial order, resulting from the molecular biaxiality, is strong.

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 or density modulation (like smectics), a polarization field or 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 approach which, as far as possible, refers to the symmetry of the order parameters.

It is a purpose of this presentation to show such an approach to study properties of biaxial systems, described in terms of the tensor- and the vector order parameters. The analysis seems important for the future, chemical synthesis of "truly" biaxial molecular fluids with chiral and possibly also polar centers. These may lead to new class of biaxial phases, described below, where some of them will probably be polar.

THEORY

Long-range orientational order in biaxial liquid crystals is described in terms of a symmetric and traceless tensor order parameter field $\underline{\underline{Q}}(\mathbf{r})$ of cartesian components $Q_{\alpha\beta}(\mathbf{r})$. By definition, the tensor vanishes in the isotropic phase while in the more ordered phases (the uniaxial nematic, smectic A, etc.) it has a cylinder symmetry about the eigenvector of $\underline{\underline{Q}}$ corresponding to the nondegenerate eigenvalue. In the most general case, when all eigenvalues are different, $\underline{\underline{Q}}(\mathbf{r})$ describes the so called general biaxial phase.[1,5,6]

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

$$[\ \underline{\underline{Q}}\ ]_{\mathrm{diag}} = \sqrt{\frac{2\sqrt{5}}{3}}\ Q\cos(\tfrac{\phi}{3}) \begin{pmatrix} \frac{1}{2}(-1-\chi) & 0 & 0 \\ 0 & \frac{1}{2}(-1+\chi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \text{(1a)}$$

where

$$\chi = \sqrt{3}\ \mathrm{tg}(\tfrac{\phi}{3}) \quad (-\pi \le \phi \le \pi\ ) \qquad \text{(1b)}$$

with $\cos(\phi) = w$, $Q^2 = \frac{1}{\sqrt{5}}\mathrm{Tr}\underline{\underline{Q}}^2$ and $w^2 = 6(\mathrm{Tr}\underline{\underline{Q}}^3)^2/(\mathrm{Tr}\underline{\underline{Q}}^2)^3$.

Maximal biaxiality is present for w = 0, i.e. for $Tr\underline{\underline{Q}}^3 = 0$.

Note that $\underline{\underline{Q}}$ does not include any long-range order of centers of mass or of dipole moments of the molecules. The ordering due to the presence of external electric or magnetic fields is also disregarded.

Description of these phenomena requires the introduction of, at least one, additional vector field **P(r)** of components $P_\alpha(\mathbf{r})$. Then, in case of polar liquid cystals **P(r)** is interpreted as a dipole density while for smectics **P(r)** is a measure of density modulation, described in terms of derivatives of the local density of mass $\rho(\mathbf{r})$: $P_\mu(\mathbf{r}) = \partial_\mu\rho(\mathbf{r})$. In the presence of an external electric or magnetic field **P(r)** = **E** or **P(r)** = **H**, respectively.

Theoretical studies of physical properties of the systems described in terms $Q_{\alpha\beta}$ and P_α require the knowledge of the nonequilibrium free energy density. This can be found from a microscopic, density functional theory or defined phenomenologically in terms of a Landau-Ginzburg expansion. In both cases the following general theorems hold[6] provided that the free energy density is an analytical function of $Q_{\alpha\beta}$ and P_α.

Theorem 1. Any analytical in $Q_{\alpha\beta}$ and P_β, **SO(3)**-symmetric nonequilibrium free energy density is a polynomial of six invariants

$$I_{02} = Tr\underline{\underline{Q}}^2 = \sqrt{5}\, Q^2 \tag{2a}$$

$$I_{03} = Tr\underline{\underline{Q}}^3 \tag{2b}$$

$$I_{20} = P_\alpha P_\alpha = \sqrt{3}\, P^2 \tag{2c}$$

$$I_{21} = P_\alpha Q_{\alpha\beta} P_\beta \tag{2d}$$

$$I_{22} = P_\alpha Q^2_{\alpha\beta} P_\beta - \tfrac{1}{3}\, Tr(\underline{\underline{Q}}^2)\, P_\alpha P_\alpha \tag{2e}$$

and

$$I_{33} = P_\alpha P_\beta P_\gamma\, \varepsilon_{\alpha\mu\nu}\, Q_{\mu\beta} Q^2_{\nu\gamma} \tag{2f}$$

where

$$108\,(I_{33})^2 = -\,54\,I_{02}\,I_{20}\,(I_{22})^2 + 54\,I_{02}\,(I_{21})^2\,I_{22} - 9\,(I_{02})^2\,(I_{21})^2\,I_{20} + 2\,(I_{02})^3\,(I_{20})^3 - 36\,I_{03}\,(I_{21})^3 + 108\,I_{03}\,I_{21}\,I_{22}\,I_{20} - 12\,(I_{03})^2\,(I_{20})^3 - 108\,(I_{22})^3\,, \tag{2g}$$

From the above theorem it follows that an arbitrary free energy expansion, which is analytical in the components $Q_{\alpha\beta}$ and P_α is a polynomial in $I_{\alpha\beta}$ and, at most, a linear function in I_{33}. Higher powers of I_{33} are eliminated by the relation (2g).

There exist further restrictions on the values of the invariants (2).

Theorem 2. For P ≠ 0 and Q ≠ 0, Eqs.(2a,c) the invariants (2) are subject to the following set of inequalities:

$$-1 \le w = \sqrt{6}\,I_{03} / (I_{02})^{3/2} \le 1 \tag{3a}$$

$$-1 \le w_1 = \sqrt{3}\,I_{21} / [\sqrt{2}\,I_{20}\,(I_{02})^{1/2}] \le 1 \tag{3b}$$

$$-1 \le w_2 = 3\,I_{22} / (I_{20}\,I_{02}) \le 1 \tag{3c}$$

$$-1 \le w_3 = -\sqrt{30}\,I_{33} / [(1 - w^2)\,(I_{02})^3\,(I_{20})^3]^{1/2} \tag{3d}$$

where w_3 is related to w, w_1 and w_2 through the equation

$$5 + 30ww_1w_2 + 30w_1^2w_2 - 5w^2 - 20ww_1^3 - 15w_1^2 - 10w_2^3 - 15w_2^2 - 9(1-w^2)w_3^2 = 0. \tag{4a}$$

and where the variables w_1, w_2 and w belong to a three dimensional volume Ω, (fig.1), embedded in a cube (w_1, w_2, w) of edge length 2. A cross section of Ω for constant w, fig.(1), is a triangle whose sides fulfill the equation

$$w_2 = Aw_1 + (1 - A^2)/2 \tag{4b}$$

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

$$w = A(3-A^2)/2 \ , \ |A| < 2. \tag{4c}$$

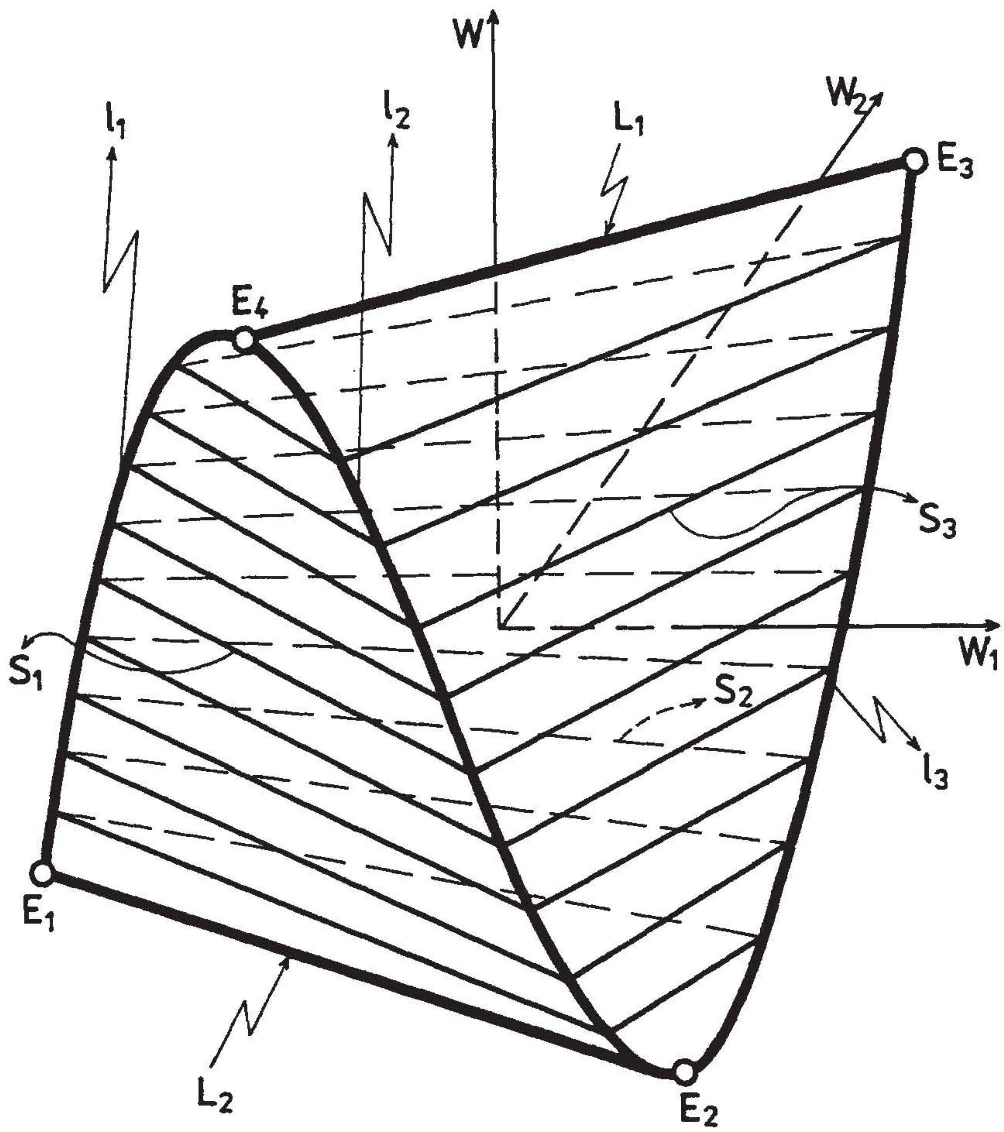


FIGURE 1. Allowed variation of the independent degrees of freedom w, w_1 and w_2. The identification of various points, arcs and surfaces is given in Table 1.

In the limiting case of $w = 1$ (-1) the triangle degenerates to an interval $w_2 = w_1$ $(-w_1)$ where $-0.5 \le w_1 \le 1$ $(-1 \le w_1 \le 0.5)$. 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 Ω unchanged and expresses a symmetry between oblate and prolate states.

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

$$2w_1^{\,2} - 1 \le w_2 \le \tfrac{1}{2}\,(w_1^{\,2} + 1). \tag{4d}$$

obtained by projecting the edges

$$\{w,\ w_1,\ w_2\} = \left\{\ 4w_1^3 - 3w_1,\ w_1,\ 2w_1^2 - 1\ \right\} \tag{4e}$$

and

$$\{w,\ w_1,\ w_2\} = \left\{\ \frac{3w_1 - w_1^3}{2},\ w_1,\ \frac{w_1^2 + 1}{2}\ \right\}, \tag{4f}$$

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 triple w,w_1,w_2 out of the interior of Ω the value of $w_3^{\,2}$ is found from eq.(4a).

From the theorem 2 it follows that the free energy depends effectively on the norms P, Q and the variables w, w_1, w_2, w_3. Since a variation of the norms ($P \neq 0$, $Q \neq 0$) does not change symmetry of a local structure the whole information about the broken symmetry states is contained in the variables w, w_1, w_2 and w_3. In order to learn something about these states it is thus enough to study geometrical properties of Ω (see fig.1). Stability range for different structures is obtained by minimization of the free energy with respect to the norms and the w's in the admitted range and under the constraint (4a).

Geometrical properties of Ω can easily be inferred from the formulas (3,4) and from the fig.1. One finds that the volume Ω can be divided into five distinct strata (see fig.1), characterized by their dimension: *i)* zero- dimensional edges $E = \{E_1, E_2, E_3, E_4\}$; *ii)* one- dimensional intervals $L = \{L_1, L_2\}$; *iii)* one- dimensional curves $l = \{l_1, l_2\}$; *iv)* two- dimensional interiors $s = \{s_1, s_2, s_3\}$ of side surfaces of Ω ($s = \partial\Omega \setminus \{E \cup L \cup l\}$) and *v)* three-dimensional interior $\Omega \setminus \partial\Omega$ of the volume Ω.

Note that these strata fully characterize geometrical structure of Ω. Except the edges E, which are isolated points, each member of a stratum represents maximal differentiable submanifold of Ω. Thus the minimization of the free energy with respect to w, w_1, w_2 (with P and Q nonzero and fixed) must be carried out separately on each stratum. Consequently one may expect that strata characterize states of different symmetry. Indeed, a system described in terms of $Q_{\alpha\beta}$ and P_β, with $Q \neq 0$ and $P \neq 0$, leads to five different local nematic structures:

1) States belonging to the surface $\partial\Omega$ of Ω.

For all states from the surface $\partial\Omega$ of Ω the I_{33} invariant vanishes ($I_{33}(\partial\Omega) = 0$). We can distinguish four groups of states (see table 1): a) a uniaxial, polar nematic state ($\mathbf{F_{U1}}$), corresponding to points E of fig.(1). The polarization is parallel to the local director; b) a uniaxial state, $\mathbf{F_{U2}}$, 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 local ordering. These states are located on the intervals L (fig.1) with exclusion of points E. c) a biaxial nematic state ($\mathbf{F_{B||}}$) with polarization parallel to one of the main tensor directions. All states with this property are located on curves l, fig.(1), with exclusion of points E;

d) a biaxial, polar nematic state ($\mathbf{F_{Bg}}$) with polarization in a plane spanned by two eigenvectors of $Q_{\alpha\beta}$. These states cover the surface $\partial\Omega$ except the points E, the intervals L and the curves l.

2) States of the interior $\Omega \setminus \partial\Omega$ of the volume Ω.

For these states the invariant I_{33} is nonzero. As upon

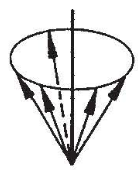
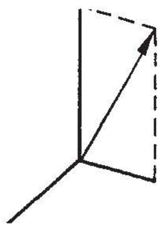
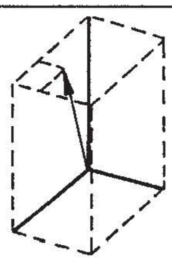
Structure	Localization (see fig.1)	Graphical representation	Relevant Invariant
F_{U1}	E_1, E_2, E_3, E_4		I_{12}
F_{U2}	L_1, L_2		I_{22}
$F_{B\|\|}$	l_1, l_2, l_3		I_{12}
F_{Bg}	S_1, S_2, S_3		I_{22}
F_{Ch}	$\Omega \setminus \partial\Omega$		I_{33}

TABLE 1. Identification of polar states generated by the invariants, eqs.(2). The arrowless lines represent nondegenerate main directions of the tensor $\underline{\underline{Q}}$. The arrows represent the orientation of the polarization vector **P** with respect to the main directions of $\underline{\underline{Q}}$.

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"(F_{Ch}). The direction of **P** 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 and chiral (otherwise the invariant I_{33} is zero).

CONCLUSIONS

In order 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, constructed from the invariants (2), and of the elastic free energy density involving gradients of **P** and $\underline{Q}$. The interpretation of the results depends strongly on the meaning of the vector field **P**. In particular, if **P** is the polarization density, the theory predicts different polar states of nematics. In addition to the uniaxial and biaxial ferroelectric nematic states, there exists a biaxial chiral ferroelectric nematic state, F_{Ch}, which is selected by the I_{33} invariant. The F_{Ch}-state differs from others in that it disappears in the limit of uniaxial, nonchiral interactions. 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 ii) large molecular biaxiality, probably of the same order as the one has observed in thermotropic biaxial nematics.

Similar statements hold for the smectic - C^* phase. One finds[6] that if the S_C* phase is stabilized due to the piezoelectric coupling between **P** and a density wave then it must be described as a biaxial, uniform spiral with, at least, two nonvanishing commensurate harmonics. Since the polarization in the S_C* phase is perpendicular to the local director, additionally the biaxial piezoelectric coupling invariant I_{33} must vanish (see Table 1).

For nonzero value of the I_{33} invariant another phase with the S_C* symmetry may be more stable. In this phase, which has locally the F_{ch} structure, the polarization is not perpendicular to the local director. Intrinsic biaxiality of the chiral molecules is the driving force, stabilizing this phase.

If **P** is interpreted as the density gradient, then, for smectics, only the cross-coupling invariants I_{21} and I_{22} are nonzero. The I_{33} invariant vanishes due to the global gauge symmetry of the smectic coupling. Clearly, the I_{21} invariant stabilizes smectic-A phases (uniaxial and biaxial) while the I_{22} invariant is responsible for the smectic - C ordering.

Finally, if **P** is interpreted as electric- or magnetic field then the invariants I_{22} and I_{33} contribute to nonlinear susceptibilities, where I_{33} is nonzero only for chiral systems and for **P** = **E**.

A thorough discussion of the phase diagrams for the cases discussed above will be presented elsewhere.

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