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Integrity basis approach to the elastic free energy functional of liquid crystals

I. Classification of basic elastic modes

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Using the method integrity basis, the most general SO(3)-invariant free energy density up to all powers in $Q_{\alpha\beta}$ and up to second order in $Q_{\alpha\beta,\gamma}$ is established. The method provides all analytically independent elastic modes for nematics and cholesterics in the form of 33 so-called, irreducible invariants. Interestingly, among the irreducible invariants there are only three chiral terms (i.e. linear in $Q_{\alpha\beta,\gamma}$). They give rise locally to three independent helix modes in chiral, biaxial liquid crystals. This conclusion generalizes results of Trebin and Govers and Vertogen and contradicts a statement of Pleiner and Brandt, according to which only one twist term is supposed to exist. The most general free energy expansion can be written as sum of 39 additive invariants, which are multiplied by arbitrary polynomials in $\mathrm{Tr}\,\mathbf{Q}^2$ and $\mathrm{Tr}\,\mathbf{Q}^3$.

1. Introduction

The orientational properties of liquid crystals can be described by a second order symmetric and traceless tensor order parameter $\mathbf{Q}(\mathbf{r})$ of cartesian components $Q_{\alpha\beta}(\mathbf{r})$ ($\alpha, \beta = x, y, z$). In the most general case $\mathbf{Q}(\mathbf{r})$ has five independent components which describe the so-called general biaxial phase [1]. A spatial dependence of $\mathbf{Q}$ requires elastic terms in the Landau free energy expansion. Together with the thermal contribution the elastic terms form the orientational part of the free energy density of liquid crystals.

De Gennes [1] was the first to propose a Landau–Ginzburg type of expansion for the free energy density in terms of $\mathbf{Q}$ and its derivatives $Q_{\alpha\beta,\gamma}$. In the absence of electric and magnetic fields, the original expression for the free energy is

$$\begin{aligned} F = {} & F_0 + a(T - T^*)\mathrm{Tr}\,\mathbf{Q}^2 + B\,\mathrm{Tr}\,\mathbf{Q}^3 + C(\mathrm{Tr}\,\mathbf{Q}^2)^2 \\ & + L_1 Q_{\alpha\beta,\gamma} Q_{\alpha\beta,\gamma} + L_2 Q_{\alpha\beta,\beta} Q_{\alpha\gamma,\gamma} \\ & + L_3 \varepsilon_{\alpha\beta\gamma} Q_{\alpha\varrho} Q_{\beta\varrho,\gamma}, \end{aligned} \tag{1}$$

where the parameters a, B, C, L_i ($i = 1$–3) are assumed to be independent of temperature. Here $\varepsilon_{\alpha\beta\gamma}$ denotes the Levi-Civita tensor. Summation over repeated indices is to be understood if not stated otherwise. The last term in equation (1) is denoted chiral. It violates parity and is responsible for the formation of a helical ground state. It appears in the elastic free energy density of cholesteric liquid crystals.

The expansion (1), though already complicated, is still too simple to describe correctly elastic and thermodynamic properties of real nematic and cholesteric liquid crystal materials [2–6]. A possible improvement is to include in equation (1) higher order terms like $\mathbf{QQ}\ldots\mathbf{Q}(\partial\mathbf{Q})$ and $\mathbf{QQ}\ldots\mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$. These symbols denote a class of all linearly independent SO(3)- symmetric invariants constructed from the tensors $Q_{\alpha\beta}Q_{\gamma\beta}\ldots Q_{\varrho\sigma}(Q_{\mu\nu,\eta})$ and $Q_{\alpha\beta}Q_{\gamma\delta}\ldots Q_{\varrho\sigma}(Q_{\mu\nu,\eta})(Q_{\xi\tau,\zeta})$ by means of contractions with the Kronnecker deltas and the Levi–Civita tensors. Such a programme has partially been carried out by Schiele and Trimper [7] and has been generalized further by Berreman and Meiboom [8] and Poniewierski and Sluckin [9]. These theories apply, in principle, to strictly uniaxial liquid crystals.

In a recent paper [6] we generalized the theories [7–9] to the biaxial case by enumerating all elastic terms up to forth order in $\mathbf{Q}$ and by changing to the spherical representation for $Q_{\alpha\beta}$ and $\partial_\mu Q_{\alpha\beta}$. The spherical representation has been used to take into account the restrictions $Q_{\alpha\alpha} = 0$, $Q_{\alpha\alpha,\beta}$ which cannot be easily incorporated into the cartesian picture. However, in orders higher than four in $\mathbf{Q}$, the use of the spherical representation also becomes very complicated. The aim of this paper is to show yet another way of expanding the elastic free energy of liquid crystals using the spherical representation. The method is based on a group theoretical construction called an integrity basis [10].

Rewriting the free energy in terms of an integrity basis offers four important advantages:

(i) the expansion is given immediately to an arbitrary order in $\mathbf{Q}$;
(ii) the analytical independence of the various terms is evident:
(iii) a formulation is possible of the most general free energy density for systems of prescribed symmetry;

and finally

(v) a classification is offered of basic elastic modes of $\mathbf{Q}$.

Furthermore we are going to show that locally the general biaxial phase can be described using only three chiral terms.

2. SO(3)-symmetric integrity basis for the liquid crystal order parameter Q

A problem often encountered in constructing a Landau–Ginzburg theory of phase transitions is to find all irreducible tensors with respect to a given discrete or compact Lie group, whose components are polynomials in the components of one or more given order parameters. These tensors are formed in terms of an integrity bases, i.e. a finite number of elementary tensors (polynomials) by which all others may be expressed as products. This very elegant group theoretical method has been developed by Judd *et al.* [10], Gaskell *et al.* [11] and Bistricky *et al.* [12].

To discuss the integrity basis for the symmetric and traceless tensor field $\mathbf{Q}$ of a liquid crystal, it is convenient to switch from cartesian to spherical components. The latter form basis functions of an irreducible representation of SO(3), namely an $L = 2$ quadrupole tensor $Q^{(2)}$ of components $Q^{(2)}_m$ ($m = \pm 2, \pm 1, 0$). The spherical components of the vector operator $\partial_i \equiv \partial/\partial x_i$ form an $L = 1$ dipole tensor $\partial^{(1)}_m$ ($m = \pm 1, 0$) [13, 14]. In the spherical representation all components $Q^{(2)}_m$ are independent, and the constraints $Q_{\alpha\beta} = Q_{\beta\alpha}$, $\mathrm{Tr}\,\mathbf{Q} = 0$ of the cartesian representation are automatically taken into account.

The problem now is to determine all irreducible SO(3)-symmetric tensors, whose components are homogeneous polynomials in $Q_m^{(2)}$. Next, by classifying the components of the derivatives $\partial\mathbf{Q}$ and $(\partial\mathbf{Q})(\partial\mathbf{Q})$ according to the irreducible representations of SO(3) and by coupling them with the irreducible tensors we can form all (analytically) independent SO(3) invariants for the free energy density.

As we have indicated an essential step is the determination of an integrity basis for the irreducible tensors. The information about these tensors and the basis is contained in a generating function $G(q, \Lambda)$ [10]. It is a rational expression, whose numerator and denominator are polynomials in variables q and Λ. The expansion of G in a power series contains only positive integer coefficients. The coefficients provide the number of linearly independent irreducible tensors of order n and momentum L. The information about the integrity basis is contained in a specific, rational form of $G(q, \Lambda)$. In particular, for $Q_m^{(2)}$ the result is [11]

$$
\begin{aligned}
G(q, \Lambda) &= \frac{1 + q^3\Lambda^3}{(1 - q\Lambda^2)(1 - q^2\Lambda^2)(1 - q^2)(1 - q^3)}, \qquad (2a)\\
&= 1 + q\Lambda^2 + q^2(\Lambda^0 + \Lambda^2 + \Lambda^4)\\
&\quad + q^3(\Lambda^0 + \Lambda^2 + \Lambda^3 + \Lambda^4 + \Lambda^6) + \ldots, \quad |\Lambda| < 1.
\end{aligned}
$$

The rational form of the generating function $(2a)$ may be interpreted in terms of five elementary tensors $I_N^{(L)}$ whose orders N and momenta L are respectively $(N, L) = (1, 2), (2, 2), (2, 0), (3, 0), (3, 3)$ where N corresponds to the powers of q, and L to the powers of Λ in the denominator and numerator of equation $(2a)$. These tensors are

$$
\left.
\begin{aligned}
I_1^{(2)} &\equiv Q^{(2)},\\
I_2^{(2)} &= [Q^{(2)} \otimes Q^{(2)}]^{(2)},\\
I_2^{(0)} &\equiv I_2 = [Q^{(2)} \otimes Q^{(2)}]^{(0)} \propto \operatorname{Tr}\mathbf{Q}^2,\\
I_3^{(0)} &\equiv I_3 = [I_1^{(2)} \otimes I_2^{(2)}]^{(0)} \propto \operatorname{Tr}\mathbf{Q}^3
\end{aligned}
\right\} \qquad (3a)
$$

and

$$
I_3^{(3)} = [I_1^{(2)} \otimes I_2^{(2)}]^{(3)} = -\frac{\sqrt{5}}{\sqrt{2}}[Q^{(2)} \otimes [Q^{(2)} \otimes Q^{(2)}]^{(4)}]^{(3)},
$$

where

$$
[T^{(l)} \otimes S^{(k)}]_m^{(L)} = \sum_{m_1, m_2} \begin{pmatrix} l & k & L \\ m_1 & m_2 & m \end{pmatrix} T_{m_1}^{(l)} S_{m_2}^{(k)} \qquad (3b)
$$

is the SO(3)-Clebsch–Gordan coupling.

Now, using equations $(3a, b)$ we can construct an infinite set of tensors of the form

$$
(I_2)^m (I_3)^n \left[\left[\bigotimes_{i=1}^{n_1} I_1^{(2)}\right]^{(2n_1)} \otimes \left[\bigotimes_{j=1}^{n_2} I_2^{(2)}\right]^{(2n_2)}\right]^{(2n_1+2n_2)}, \qquad (3c)
$$

$$
(I_2)^m (I_3)^n \left[I_3^{(3)} \otimes \left[\left[\bigotimes_{i=1}^{n_1} I_1^{(2)}\right]^{(2n_1)} \otimes \left[\bigotimes_{j=1}^{n_2} I_2^{(2)}\right]^{(2n_2)}\right]^{(2n_1+2n_2)}\right]^{(2n_1+2n_2+3)}, \qquad (3d)
$$

where m, n, n_1, n_2 run over the non-negative integers and where

$$
\left[\bigotimes_{i=1}^{n} A^{(J)}\right]^{(nJ)} \equiv [\ldots[A^{(J)} \otimes [A^{(J)} \otimes A^{(J)}]^{(2J)}]^{(3J)} \ldots]^{(nJ)}. \qquad (3e)
$$

The set of the tensors (3c, d) corresponds formally to the representation of the generating function (2a, b) as

$$(1 + \Lambda^3 q^3) \sum_{m,n,n_1,n_2} (q^2)^m (q^3)^n (q\Lambda^2)^{n_1} (q^2\Lambda^2)^{n_2}$$
$$= \frac{1 + q^3\Lambda^3}{(1 - q\Lambda^2)(1 - q^2\Lambda^2)(1 - q^2)(1 - q^3)}.$$

These tensors are irreducible and linearly independent. Note that the tensor $I_3^{(3)}$, associated with the term $q^3\Lambda^3$, can appear only linearly in equation (3d). The higher order couplings of this tensor with itself can be expressed as Clebsch–Gordan couplings of integrity basis elements (3a).

Finally, we note that any other tensor formed by means of coupling of several tensors $Q^{(2)}$ can be expressed uniquely as a linear combination of the tensors (3c, d). For example,

$$[I_1^{(2)} \otimes I_2^{(2)}]^{(2)} = \frac{2\sqrt{5}}{7} I_2 Q^{(2)}.$$

3. Invariant expansion of the free energy

In the previous section we listed all of the linearly independent, irreducible tensors constructed from $Q^{(2)}$. Here we apply these results to construct systematically a general free energy expansion in terms of $\mathbf{Q}$ and its derivatives $Q_{\alpha\beta,\gamma}$. Only terms, that are linear or quadratic in derivatives of $\mathbf{Q}$ are considered, i.e. we restrict the expansion to the SO(3)-symmetric invariants of the form $\mathbf{QQ} \ldots \mathbf{Q}(\partial\mathbf{Q})$ and $\mathbf{QQ} \ldots \mathbf{Q}(\partial\mathbf{Q})(\partial\mathbf{Q})$ or equivalently, using spherical tensor notation

$$\left[\left[\bigotimes_{i=1}^{n} Q^{(2)}\right]^{(L)} \otimes \partial Q^{(L)}\right]^{(0)}$$

and

$$\left[\left[\bigotimes_{i=1}^{n} Q^{(2)}\right]^{(L)} \otimes [\partial Q^{(L_1)} \otimes \partial Q^{(L_2)}]^{(L)}\right]^{(0)}, \tag{4b}$$

where

$$\partial Q^{(L)} \equiv [\partial^{(1)} \otimes Q^{(2)}]^{(L)}, \quad L = 1, 2, 3. \tag{4c}$$

The structure of the tensor space $\left[\bigotimes_{i=1}^{n} Q^{(2)}\right]^{(L)}$ has already been studied (see equations (3c, d)). Thus, it remains to identify all of the linearly independent, irreducible representations $\partial Q^{(L)}$ and $[\partial Q^{(L_1)} \otimes \partial Q^{(L_2)}]^{(L)}$. First we note that $\partial^{(1)}$ and $Q^{(2)}$

Table 1. Irreducible representations (L_1, L_2, L).

L_1	L_2	L
1	1	0 2
1	2	1 2 3
1	3	2 3 4
2	2	0 2 4
2	3	1 2 3 4 5
3	3	0 2 4 6

Table 2. Chiral (J) and quadratic in $\partial\mathbf{Q}$ (D) invariants. These are formed by all possible couplings of the terms in the left column with the corresponding terms in the right column to give a total momentum L of zero. Invariants which can be replaced by $J_\alpha J_\beta$ are underlined. ($\partial Q^{(L)} \equiv [\partial^{(1)} \otimes Q^{(2)}]^{(L)}$).

Couplings of $\partial Q^{(M)}$ and its square to total angular momentum L	Coupling of powers of $Q^{(2)}$ to the same angular momentum L as on left side via the method of integrity basis
	J-Invariants
$\begin{matrix}1\text{ times}\\ L=2\end{matrix}\ \{\partial Q^{(2)}\}$	$\begin{matrix}2\text{ times}\\ L=2\end{matrix}\ \left\{\begin{matrix}Q^{(2)}\\ I_2^{(2)}\end{matrix}\right\}$ 2 irreducible invariants
$\begin{matrix}1\text{ times}\\ L=3\end{matrix}\ \{\partial Q^{(3)}\}$	$\begin{matrix}1\text{ times}\\ L=1\end{matrix}\ \{I_3^{(3)}\}$ 1 irreducible invariant
	D-Invariants
$\begin{matrix}3\text{ times}\\ L=0\end{matrix}\ \left\{\begin{matrix}[\partial Q^{(1)} \otimes \partial Q^{(1)}]^{(0)}\\ [\partial Q^{(2)} \otimes \partial Q^{(2)}]^{(0)}\\ [\partial Q^{(3)} \otimes \partial Q^{(3)}]^{(0)}\end{matrix}\right\}$	$\begin{matrix}1\text{ times}\\ L=0\end{matrix}\ \{1\}$ 3 irreducible invariants
$\begin{matrix}6\text{ times}\\ L=2\end{matrix}\ \left\{\begin{matrix}[\partial Q^{(1)} \otimes \partial Q^{(1)}]^{(2)}\\ [\partial Q^{(1)} \otimes \partial Q^{(2)}]^{(2)}\\ [\partial Q^{(1)} \otimes \partial Q^{(3)}]^{(2)}\\ [\partial Q^{(2)} \otimes \partial Q^{(2)}]^{(2)}\\ [\partial Q^{(2)} \otimes \partial Q^{(3)}]^{(2)}\\ [\partial Q^{(3)} \otimes \partial Q^{(3)}]^{(2)}\end{matrix}\right\}$	$\begin{matrix}2\text{ times}\\ L=2\end{matrix}\ \left\{\begin{matrix}Q^{(2)}\\ I_2^{(2)}\end{matrix}\right\}$ 12 irreducible invariants
$\begin{matrix}3\text{ times}\\ L=3\end{matrix}\ \left\{\begin{matrix}[\partial Q^{(1)} \otimes \partial Q^{(2)}]^{(3)}\\ [\partial Q^{(1)} \otimes \partial Q^{(3)}]^{(3)}\\ [\partial Q^{(2)} \otimes \partial Q^{(3)}]^{(3)}\end{matrix}\right\}$	$\begin{matrix}1\text{ times}\\ L=3\end{matrix}\ \{I_3^{(3)}\}$ 3 irreducible invariants
$\begin{matrix}4\text{ times}\\ L=4\end{matrix}\ \left\{\begin{matrix}[\partial Q^{(1)} \otimes \partial Q^{(3)}]^{(4)}\\ \underline{[\partial Q^{(2)} \otimes \partial Q^{(2)}]^{(4)}}\\ [\partial Q^{(2)} \otimes \partial Q^{(3)}]^{(4)}\\ [\partial Q^{(3)} \otimes \partial Q^{(3)}]^{(4)}\end{matrix}\right\}$	$\begin{matrix}3\text{ times}\\ L=4\end{matrix}\ \left\{\begin{matrix}\underline{[Q^{(2)} \otimes Q^{(2)}]^{(4)}}\\ \underline{[Q^{(2)} \otimes I_2^{(2)}]^{(4)}}\\ \underline{[I_2^{(2)} \otimes I_2^{(2)}]^{(4)}}\end{matrix}\right\}$ 12 irreducible invariants
$\begin{matrix}1\text{ times}\\ L=5\end{matrix}\ \underline{\{[\partial Q^{(2)} \otimes \partial Q^{(3)}]^{(5)}\}}$	$\begin{matrix}2\text{ times}\\ L=5\end{matrix}\ \left\{\begin{matrix}\underline{[Q^{(2)} \otimes I_3^{(3)}]^{(5)}}\\ \underline{[I_2^{(2)} \otimes I_3^{(3)}]^{(5)}}\end{matrix}\right\}$ 2 irreducible invariants
$\begin{matrix}1\text{ times}\\ L=6\end{matrix}\ \underline{\{[\partial Q^{(3)} \otimes \partial Q^{(3)}]^{(6)}\}}$	$\begin{matrix}4\text{ times}\\ L=6\end{matrix}\ \left\{\begin{matrix}[Q^{(2)} \otimes Q^{(2)} \otimes Q^{(2)}]^{(6)}\\ [Q^{(2)} \otimes Q^{(2)} \otimes I_2^{(2)}]^{(6)}\\ [Q^{(2)} \otimes I_2^{(2)} \otimes I_2^{(2)}]^{(6)}\\ \underline{[I_2^{(2)} \otimes I_2^{(2)} \otimes I_2^{(2)}]^{(6)}}\end{matrix}\right\}$ 4 irreducible invariants

can be coupled to obtain three independent irreducible representations with $L = 1$, 2, 3 (see equation (4 c)). Now studying the second case (see equation (4 b)) and observing correctly the permutation symmetry with respect to $\partial Q^{(L)}$, we find that various irreducible representations (L_1, L_2, L) can be classified as given in table 1. Clearly, by combining these results with those of the previous section we find there are 39 invariants (4 a, b); these are listed in table 2. Not all of the couplings between spherical tensors (3 c, d) and the derivatives $[\partial Q^{(M)} \otimes \partial Q^{(N)}]^{(L)}$ to give a total momentum of zero are analytically independent. Six of them, underlined in table 2, can be expressed as polynomials of invariants of lower order.

We conclude that the general free energy density of cholesteric liquid crystals is composed of 3 J_α-invariants, 6 $J_\alpha J_\beta$-invariants and 30 D-invariants. These can be multiplied by arbitrary polynomials in I_2 and I_3 (see equations (3 c, d)).

Interestingly, the theory predicts a finite number of elementary distortion modes in a general, biaxial system corresponding to the three J_α-invariants and the 30 D-invariations. Among the allowed distortions there are *only three types of chiral ones* and this number cannot be reduced for biaxial phases. This result generalizes that of Trebin [15] and of Govers and Vertogen [16] and contradicts that of Pleiner and Brandt [17]. They argue that the ground state of a chiral biaxial nematic must consist of a single helix formation and that the description of such a state involves only one twist term. According to the theory presented here elastic terms with J_1 or J_2 give rise to different local structures than J_3 so a ground state with single helix is impossible if these terms compete.

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