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INTEGRITY BASES AND THE STRUCTURE OF ORDER PARAMETER SPACE.

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Dedicated to Prof. Dr E.Kröner *on the occasion of his 70th birthday*

Abstract The mathematical concept of integrity bases was coined by Molien and Hilbert about one hundred years ago to characterize the algebra of invariants of a finite group. The field has latter been generalized to obey the case of the compact Lie groups. In particular, it has been shown that for orientational order parameters which transform like irreducible representations of SO(3) it is possible to construct a finite number of (algebraically) independent invariant polynomials (integrity basis) build out of the components of the order parameters, such that all other invariants can be written as polynomials of these basic invariants.

Here it is demonstrated on some simple examples how to apply this theorem to study a) elastic free energies and b) topologies of phase diagrams in molecular- and Landau theories of liquid crystals. Mathematical background and references sufficient for extensions of the results are also given.

INTRODUCTION

The transition between phases of different symmetry can be described in terms of the so called 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.

In general, many order parameters are needed to characterize orientational properties of a liquid crystal. However, from a unique order parameter set we may always

select primary ones to which the other (secondary ones) my be slaved. A standard way of finding the primary order parameters of liquid crystals is by referring to the one-particle distribution function[1] or to the macroscopic response functions of the bulk material[2-4].

Most of the phases in which only orientational degrees of freedom condense, are biaxial. These include the experimentally observed chelicoidal (cholesteric) phase[2], blue phases[5] and a recently discovered thermotropic biaxial nematics[6].

For biaxial phases the primary orientational order parameter is often identified with a second-order, symmetric and traceless tensor field $\underline{Q}$ of cartesian components $Q_{\alpha\beta}$ (α,β = x,y,z), where the case $Q_{\alpha\beta}=0$ corresponds to the isotropic phase. For uniaxial phases two out of three eigenvalues of $\underline{Q}$ are equal which requires that $6(\mathrm{Tr}\underline{Q}^3)^2 = (\mathrm{Tr}\underline{Q}^2)^3$. In the case of general biaxial phase $\underline{Q}$ has five independent components.

For many applications it is convenient to switch from the cartesian representation for $Q_{\alpha\beta}$ to the spherical one as the latter defines the irreducible representations of SO(3). In this representation the spherical components $Q^{(2)}_m$ (m = ±2, ±1, 0) of $\underline{Q}$ form an L=2 quadrupole tensor $Q^{(2)}$

$$
\begin{aligned}
Q^{(2)}_{\pm 2} &= -\frac{1}{2}(Q_{xx} - Q_{yy} \pm 2iQ_{xy}) \\
Q^{(2)}_{\pm 1} &= \pm(Q_{xz} \pm iQ_{yz}) \qquad (1) \\
Q^{(2)}_{0} &= \frac{3}{\sqrt{6}}(Q_{xx} + Q_{yy}).
\end{aligned}
$$

An important advantage of use of spherical representation is that all components $Q^{(2)}_m$ are independent, and the constraints $Q_{\alpha\beta} = Q_{\beta\alpha}$, $Q_{\alpha\alpha} = \mathrm{Tr}\underline{Q} = 0$, and $\partial_\mu Q_{\alpha\alpha} = 0$ of the cartesian representation are automatically taken regard of.

In molecular theories of biaxial phases one may need more complicated primary order parameters like the average

values of the Wigner rotation matrices of rank L=2, $\langle D^{(2)}_{m,n} \rangle$, or the polar tensors $P^{(1)}_{m}$ ($\equiv Q^{(1)}_{m}$). Secondary order parameters are used to approximate the distribution function more precisely. For nonpolar nematics these are given by irreducible tensors $Q^{(2L)}_{m}$ or $\langle D^{(2L)}_{m,n} \rangle$ ($L > 1$).

A physical, SO(3)-symmetric theory, which is analytical in the order parameters $T^{(1)}$ and $S^{(k)}$, is defined as an expansion in polynomial invariant or covariant vector fields build out of components of $T^{(1)}_{m}$ and $S^{(k)}_{q}$. In particular, molecular-, Landau- or elastic theories of liquid crystals can be viewed as linear combinations of SO(3) invariant polynomials i.e. spherical products with total momentum L=0. These are found by means of standard Clebsch-Gordon coupling

$$Z^{(L)}_{m} = [T^{(1)} \otimes S^{(k)}]^{(L)}_{m}$$

$$:= \sum_{m_1,m_2} \begin{pmatrix} 1 & k \\ m_1 & m_2 \end{pmatrix} \begin{matrix} L \\ m \end{matrix} \Big) \; T^{(1)}_{m_1} \, S^{(k)}_{m_2} \qquad (2)$$

where $\left(\begin{matrix} 1 & k \\ m_1 & m_2 \end{matrix} \middle| \begin{matrix} L \\ m \end{matrix}\right)$ are Clebsch-Gordon coefficients and where tensors $Z^{(L)}_{m}$ transform according to the angular quantum number $L \in 1+k, 1+k-1, \ldots . |1-k|$. The formula (2) can be used recursively to form higher-order polynomials.

Our task in this presentation will be to show a systematic way of studying general properties of the theories mentioned above. This is achieved by rewriting the theory in terms of integrity bases i.e. a finite number of "elementary" tensors (polynomials) by which all other tensors may be expressed as well defined (and simple) products. This very elegant group theoretical method has been developed for finite groups by Molien[7] and recently generalized to compact Lie groups by Judd et.al.[8], Gaskell et.al[9] and Bistricky et.al.[10]. In particular, it will be demonstrated that rewriting the free energy in terms of the integrity basis offers five important advantages over

the standard treatment:

i) the expansion is given immediately to an arbitrary order;

ii) the algebraic[a] independence of the various invariants (covariants) is evident;

iii) a correlation is proposed with little groups of an SO(3)-symmetric order parameter;

iv) a very convenient parameterization is given of the free energy;

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

Moreover, the IB approach reveals new internal symmetries of the expansion, like natural hierarchical structure between various invariants.

INTEGRITY BASIS FOR VECTOR AND TENSOR FIELDS

Orientational free energy for an order parameter given by harmonic L must be rotationally invariant. This means that terms of a given degree in the free energy expansion must be separately invariant under all rotations. The total number $m_{n,0}$ of such linearly independent invariants of a given degree n can be calculated from a generating function $G(q,\Lambda)$[8-10] for SO(3) tensors contained in the symmetric product of an arbitrary number of identical SO(3) tensors.

The generating function is a rational expression (see example below) whose numerator and denominator are polynomials in q and Λ. The power series expansion of $G(q,\Lambda)$ contains only the terms with positive integer coefficients $m_{n,L}$

$$G(q,\Lambda) = \sum_{n,L} m_{n,L}\, q^{n} \Lambda^{L} \qquad (3)$$

---

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

where $m_{n,L}$ yields the number of linearly independent irreducible tensors of degree n and momentum L .

The construction of $G(q,\Lambda)$ is based on the orthogonality theorems for characters of products of irreducible representations of $SO(3)$[8-10]. The results for $L \leq 13/2$ are gathered in ref.10. Note, however, a mistake in formula (2.3) of ref.10. The term U^{3L-6} there should read A^{3L-6}. Detailed calculations for L = 6 are found in ref.11. Here we list the results for L=1 (vector field) and for L=2, eq.(2).

Vector Field L=1

For the vector field $P^{(1)}$ the generating function $G(p,\Lambda)$ reads

$$G(p,\Lambda) = \frac{1}{(1-p^2)\,(1-p\Lambda)} = \sum_{n=0} (p^2)^n \sum_{L=0} p^L\, \Lambda^L$$

From the rational form of $G(p,\Lambda)$ it follows that polynomials in $P^{(1)}_m$, transforming like $SO(3)$ irreducible representations, can be constructed using only two tensor fields $P^{(1)}$ and $P_2 = [P^{(1)} \otimes P^{(1)}]^{(0)}$. This is achieved by means of Clebsh-Gordon couplings between $P^{(1)}$ and P_2 to the highest possible total momenta

$$(P_2)^n\, [\ldots[\,[\,P^{(1)} \otimes P^{(1)}]^{(2)} \otimes P^{(1)}\,]^{(3)} \ldots .]^{(m)}.$$

These two basic tensor fields reproducing the structure of the tensor spaces formed from $P^{(1)}$ are called integrity basis (IB).

Tensor Field L=2

For $Q^{(2)}$ the result is

$$G(q,\Lambda) = \frac{1 + q^3\,\Lambda^3}{(1-q\,\Lambda^2)(1-q^2\Lambda^2)(1-q^2)(1-q^3)} \qquad (4a)$$

$$= 1 + q\Lambda^2 + q^2(\Lambda^0 + \Lambda^2 + \Lambda^4) + q^3(\Lambda^0 +$$

$$\Lambda^2 + \Lambda^3 + \Lambda^4 + \Lambda^6) + \ldots, |\Lambda|<1 \qquad (4b)$$

The rational form of the generating function (4a) may now be reproduced using five "elementary" tensors $I^{(L)}_{N}$ whose degrees N and momenta L are respectively (N,L) = (1,2), (2,2), (2,0), (3,0), (3,3). These tensors, forming the IB, can be unambiguously identified as [12,13]

$$I^{(2)}_{1} \equiv Q^{(2)} \qquad I^{(2)}_{2} = [Q^{(2)} \otimes Q^{(2)}]^{(2)}$$
$$I^{(0)}_{2} \equiv I_2 = [Q^{(2)} \otimes Q^{(2)}]^{(0)} \qquad (5a)$$
$$I^{(0)}_{3} \equiv I_3 = [I^{(2)}_{1} \otimes I^{(2)}_{2}]^{(0)}$$

and

$$I^{(3)}_{3} = [I^{(2)}_{1} \otimes I^{(2)}_{2}]^{(3)}$$
$$= -\frac{\sqrt{5}}{\sqrt{2}} [Q^{(2)} \otimes [Q^{(2)} \otimes Q^{(2)}]^{(4)}]^{(3)}. \qquad (5b)$$

Any other SO(3) - symmetric tensors built out of $Q^{(2)}$ can be decomposed in the basis which is formed by means of all possible Clebsch-Gordon couplings between an arbitrary number of tensors (5a) to the highest possible total momenta. The tensor $I^{(3)}_{3}$, eq.(5b), associated with the term $q^3\Lambda^3$ in numerator of (4a), can appear at most linearly in these couplings. Note that the order of the Clebsch-Gordon couplings is irrelevant and a given set of tensors taken from integrity basis leads to one irreducible tensor only.

APPLICATIONS TO LIQUID CRYSTALS

In the previous section we showed how to construct all linearly independent, irreducible tensors built out of $Q^{(2)}$ and $p^{(1)}$. Here we apply these results to discuss the structure of a general free energy expansion in terms of $\underline{Q}$ and its derivatives $Q_{\alpha\beta,\gamma}$ [12,13] and identify all polar structures that follow from theories based on $Q^{(2)}$ and $p^{(1)}$. We start our considerations by giving

interpretation[13] of the elements of integrity basis (5).

The integrity basis element, I_2, is the square of the norm of the order parameter $Q^{(2)}$

$$I_2 = | Q^{(2)} |^2 = \frac{1}{\sqrt{5}} \mathrm{Tr}\underline{Q}^2. \qquad (6a)$$

Thus with $\mathrm{Tr}\underline{Q}^2 = \text{const}$ we let $Q^{(2)}$ take the values out of a four-sphere in five dimensional space of $Q^{(2)}_m$.

Invariant I_3 is the scalar product of two vectors $I^{(2)}_1$ and $I^{(2)}_2$ belonging to the IB (eq.(7)) . Thus

$$(I_3)^2 = ([I^{(2)}_1 \otimes I^{(2)}_2]^{(0)})^2 = (|I^{(2)}_1||I^{(2)}_2| \cos(\phi))^2$$

$$= \frac{2\sqrt{5}}{7} (I_2)^3 \cos(\phi)^2 \leq \frac{2\sqrt{5}}{7} (I_2)^3, \qquad (6b)$$

where ϕ is the "angle" between vectors $I^{(2)}_1$ and $I^{(2)}_2$. For uniaxial phase the uniaxiality conditions can be written in terms of I_2 and I_3 as $10(I_2)^3 = 7\sqrt{5}(I_3)^2$, which means that the uniaxial phase corresponds to the case of $\phi = 0$ (oblate uniaxials) or π (prolate uniaxials). Thus the value of $\cos(\phi)^2$ can be regarded as a measure of degree of uniaxiality of a given phase. The pair of independent invariants (I_2, $\cos(\phi)$) gives natural parameterization of the Landau theory of nematics.

Qualitatively different interpretation has the $I^{(3)}_3$ element of integrity basis. We note that for uniaxial phases the vectors $I^{(2)}_1$ and $I^{(2)}_2$ are either parallel ($\phi = 0$) or antiparallel ($\phi = \pi$). It means that

$$I_2 I^{(2)}_2 = \pm I_3 I^{(2)}_1. \qquad (7a)$$

Consequently, for uniaxial symmetry

$$I^{(3)}_3 = \pm \frac{I_2}{I_3} [I^{(2)}_1 \otimes I^{(2)}_1]^{(3)} = 0. \qquad (7b)$$

Thus, the $I^{(3)}_3$ vector disappears for uniaxial deformations and, consequently, its norm provides a measure of biaxiality of local distortions.

Elastic free energy[13]

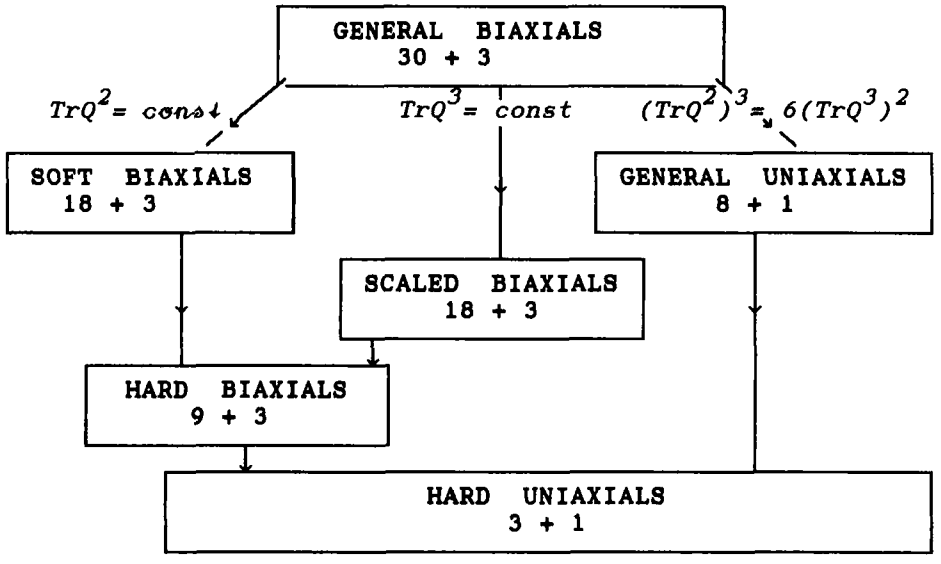
It is now straightforward to construct general free energy expansion in terms of $\underset{\sim}{Q}$ and its derivatives $Q_{\alpha\beta,\gamma}$ [58,59], or equivalently in terms of $Q^{(2)}$ and $\partial Q^{(L)} \equiv [\partial^{(1)} \otimes Q^{(2)} +]^{(L)}$, L=1,2,3. In particular, we find that there are only three types of chiral terms $[I^{(L)}_{\alpha} \otimes \partial Q^{(L)}]^{(0)}$ $(L,\alpha) = (2,1), (2,2), (3,3)$. These can be multiplied by arbitrary polynomials in I_2 and I_3. In order to find the number of elastic terms that are quadratic in derivatives we note first that the maximal L in the coupling $[\partial Q^{(M)} \otimes \partial Q^{(N)}]^{(L)}$ is 6. Consequently, only those couplings between the elements of integrity basis are relevant which when further coupled with derivatives $[\partial Q^{(M)} \otimes \partial Q^{(N)}]^{(L)}$, form an SO(3) invariant. A number of these invariants is given in Table I. All of them can again be multiplied by arbitrary polynomials in I_2 and I_3. Table I gives also the number of invariants in some limiting cases where additional restrictions are imposed on the invariants I_2 and I_3.

One of important features of the theory is that it directly refers to the internal symmetry (little group) of the order parameter and gives only algebraically independent invariants.

The last property of the integrity basis approach allows us to divide biaxial systems into five different classes as shown in Table I, where the numbers of irreducible invariants quadratic and linear in derivatives are also given for each phase. Of particular importance is the reduction of general biaxial theory to that governed by uniaxial symmetry. In this case the terms proportional to $I^{(3)}_3$ vanish and those with $I^{(2)}_1$ and $I^{(2)}_2$ are correlated via eq.(7a). Thus, for uniformly parallel equilibrium structures of nematic phases the terms with $I^{(3)}_3$ may safely be disregarded, while the elastic constants in front of the invariants with $I^{(2)}_1$ and $I^{(2)}_2$ are simply correlated.

Moreover, the theory predicts 3 types of chiral distortions and this number cannot be reduced for biaxial phases.

Table I *Different nematic phases which are derived from general biaxial case by special restrictions. Indicated are the numbers of quadratic plus linear irreducible invariants involved in the construction of the elastic free energy density for each phase.*



Polar states with nematic symmetry[14]

With the help of integrity basis one finds very convenient approach to study selection rules for broken symmetry states in an arbitrary Landau-like free energy expansion. As an example we investigate the correlation between polar nematic states and the properties of the integrity basis for invariants composed of the components of $P^{(1)}$ and $Q^{(2)}$. The analysis will be restricted to the case when $P^{(1)}$ and $Q^{(2)}$ are position independent.

The integrity basis for invariants of two order parameters $P^{(1)}$ and $Q^{(2)}$ is composed of five invariants $\Pi_{\alpha,\beta}$, whose degrees of $P^{(1)}$ and $Q^{(2)}$ are α and β,

respectively. The invariants and their Cartesian counterparts can unambiguously be identified as[14]

$$\Pi_{2,0} = P_2 , \quad \Pi_{0,2} = I_2, \quad \Pi_{0,3} = I_3,$$

$$\Pi_{2,1} = [P^{(2)} \otimes I_1^{(2)}]^{(0)} = | P^{(2)}||I_1^{(2)}|\cos\phi_1 \sim P_\alpha Q_{\alpha\beta} P_\beta$$

$$\Pi_{2,2} = [P^{(2)} \otimes I_2^{(2)}]^{(0)} = | P^{(2)}||I_2^{(2)}|\cos\phi_2$$

$$\sim P_\alpha Q^2_{\alpha\beta} P_\beta - \tfrac{1}{3} \mathrm{Tr}(Q^2)\, P^2 \qquad (8a)$$

and

$$\Pi_{3,3} = [P^{(3)} \otimes I_3^{(3)}]^{(0)} = |P^{(3)}||I_3^{(3)}|\cos\phi_3$$

$$\sim P_\alpha P_\beta P_\gamma\, \varepsilon_{\alpha\mu\nu}\, Q_{\mu\beta} Q^2_{\nu\gamma} \qquad (8b)$$

where

$$P^{(L)} = [\ldots[\,[P^{(1)} \otimes P^{(1)}]^{(2)} \otimes P^{(1)}]^{(3)} \otimes \ldots]^{(L)}$$

and where

$$| P^{(2)}|^2 = \frac{2\sqrt{5}}{5} (P_2)^2, \qquad | P^{(3)}|^2 = \frac{6\sqrt{21}}{35} (P_2)^3.$$

Any other invariant formed by means of coupling of some $P^{(1)}$ and $Q^{(2)}$ can be expressed as a polynomial of invariants (8a,b). Furthermore, the powers $(\Pi_{3,3})^n$ with $n > 1$, are polynomials of (8a,b). In particular $(\Pi_{3,3})^2$ gives

$$9(1- w^2)w_3^2 = 5 + 30ww_1w_2 + 30w_1^2w_2 - 5w^2 - 20ww_1^3 - 15w_1^2$$

$$- 10w_2^3 - 15w_2^2 \geq 9(1-w^2), \qquad (8c)$$

where $w = \cos(\phi)$ and where $w_\alpha = \cos(\phi_\alpha)$, $\alpha = 1,2,3$. Consequently, the Landau free energy expansion for polar nematics is a stable polynomial in $\Pi_{\alpha,\beta}$ and a linear function in $\Pi_{3,3}$. As $\Pi_{\alpha,\beta}$ are algebraically independent, the practical minimization of the free energy can be carried out with respect to the six invariants $| P^{(1)}|$, $|Q^{(2)}|$, w and w_α, $\alpha = 1,2,3$ under the constraint (8c).

The interpretation of the integrity basis elements and classification of resulting ferroelectric structures can easily be inferred from eqs (8). One finds that in addition to the uniaxial and biaxial ferroelectric nematic phases, the theory predicts, a biaxial chiral ferroelectric nematic phase. It is generated by the $\Pi_{3,3}$ term, eq.(8b), of the integrity basis (8). From the form of $\Pi_{3,3}$ it is clear that the following must be fulfilled for the possible existence of the F_{Bch} phase: 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 observed in thermotropic biaxial nematics[6]. The above predictions are in accordance with recent expectations that the non centrosymmetric biaxial molecules with negative dielectric anisotropy may be good candidates to form a ferroelectric, nematic-like phase(s)[15-17].

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