Electrostriction of the cubic blue phases in the presence of bond orientational order

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The cubic blue phase I displays anomalous electrostriction, i.e., if the electric field vector is rotated from one crystallographic direction to another, the deformation along the field changes from dilatation to compression or vice versa. Standard theories of blue phases based on an expansion of the free energy in powers of the alignment tensor $\boldsymbol{Q}(\boldsymbol{r})$ are not able to explain this anomaly. Cubic blue phases possess a strong nonlinear dielectric susceptibility $\boldsymbol{\chi}^4$, as shown by experiments of Pierański, Cladis, Garel, and Barbet-Massin [J. Phys. (Paris) **47**, 139 (1986)]. Hence the corresponding order parameter, which we denote ''bond orientational tensor,'' must be included in a theoretical description of the blue phases. Indeed, it has been proposed that the blue phase III is a structure of pure bond orientational order. Incorporating the bond orientational tensor into the free energy expansion, we have calculated the distortion of the $O^8(I4_132)$ and $O^2(P4_232)$ blue phase lattices by a weak electric field within the model of rigid helices. The resulting fourth-order electrostriction tensor is expressed in terms of the order parameters characterizing the O^8 and the O^2 ground states of the undistorted system. The relations generalize studies of Stark and Trebin [Phys. Rev. A **44**, 2752 (1991)]. It is found that there exists a range for the coupling strength between $\boldsymbol{Q}(\boldsymbol{r})$ and $\boldsymbol{\chi}^4$ where anomalous electrostriction is predicted for blue phase I, in accordance with experiment. Thus bond orientational order seems to provide a link between two unsolved problems: that of the anomalous electrostriction of the blue phase I and that of the structure of the blue phase III. [S1063-651X(96)02806-1]

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I. INTRODUCTION

In the absence of an electric field, as many as three distinct blue phases can appear between the isotropic liquid phase and the cholesteric phase. They are labeled, with ascending temperature, BPI, BPII, and BPIII, the latter being also denoted blue fog.

Experiments confirm that the two lower temperature phases, BPI and BPII, may be described as a body centered cubic structure with space group symmetry $O^8(I4_132)$ and a simple cubic structure with space group symmetry $O^2(P4_232)$ [1], respectively. A theoretical approach correctly identifying these structures was presented by Grebel, Hornreich, and Shtrikman [2]. However, the structure of BPIII is still a matter of intensive studies and controversy [1–4].

A weak field only slightly deforms the blue phase lattices. In the limit of a vanishing field these deformations are expressed by the electrostriction tensor $\boldsymbol{R}$, which, in turn, depends only on details of the cubic ground states. Hence a calculation of the electrostriction tensor can provide an additional test of the Grebel-Hornreich-Shtrikman (GHS) theory, at least in the temperature and chirality range where the structures of BPI and BPII are reproduced correctly. Calculations along this line have been carried out by Lubin and Hornreich [5], Dmitrienko [6], and Stark and Trebin [7]. The ratios of the independent components $R_1=R_{1111}$, $R_2=R_{1122}$, and $R_3=2R_{2323}$ of $\boldsymbol{R}$ were found in an approximation that preserves the mass density of the molecules. The authors obtained $R_1/R_2=-2$, in agreement with experiments of Heppke *et al.* [8] and Dolganov *et al.* [9]. On the other hand, Porsch and Stegemeyer [10] have measured $R_1/R_2\approx-2.6$, but this value has been questioned [9].

The ratio R_1/R_3 has been reproduced correctly for BPII, where experiments yielded values between 0.4 and 1.0. For BPI the experimental values of R_1/R_3 are *negative* and fall in the range between -0.1 and -0.4, which means that the deformations along [001] and [011] directions differ in sign. Theory, however, gives positive values similar to those obtained for BPII. This *anomalous* character of the BPI electrostriction, i.e., dilatation along one direction and compression along the other crystallographic direction, remains one of the unsolved problems of chiral liquid crystal physics.

In this article we present a possible explanation of the anomalous electrostriction by generalizing the original GHS theory. The approach is motivated by experiments of Pierański *et al.* [11], where crystals of the cubic blue phases were oriented by an electric field. It has been demonstrated that BPI and BPII possess a strong nonlinear dielectric susceptibility $\boldsymbol{\chi}^4$ of cubic symmetry. The corresponding order parameter is the $L=4$ part of $\boldsymbol{\chi}^4$, which we call the ''bond orientational tensor.'' Based on a Landau-Ginzburg free energy expansion, which incorporates this tensor in addition to the standard alignment tensor field $Q_{\alpha\beta}(\boldsymbol{r})$, the electrostriction tensor is calculated for BPI and BPII. The resulting fourth-order electrostriction tensor is expressed in terms of both the bond orientational tensor and the alignment tensor field of the undistorted system. The calculations generalize recent work of Stark and Trebin [7]. Since a similar theory has been proposed to explain the structure of the blue fog [4], our calculations seem to provide a connection between the two at first sight uncorrelated problems: that of the anomalous elec-

trostriction of BPI and that of the structure of BPIII.

The organization of this paper is as follows. In Sec. II an introduction to the Landau–Ginzburg–de Gennes theory of chiral nematic liquid crystals is given. Also a discussion of the relevant order parameters is included. Section III introduces the basic ingredients of the electrostriction theory. Within the approximation of rigid helices approximate formulas for the components of the electrostriction tensor are derived. Numerical results are presented in Sec. IV.

II. LANDAU–GINZBURG–DE GENNES THEORY OF CHOLESTERIC LIQUID CRYSTALS

The orientational properties of the molecules in the blue phases are described with the help of the Landau–Ginzburg–de Gennes theory. It is based on the concept of order parameters: quantities that measure the ordering of the system under study.

A standard way to introduce order parameters is by referring to the one-particle distribution function [12] or to macroscopic response functions of the bulk material [13] such as the dielectric permittivity $\boldsymbol{\chi}$. Consider, for instance, the polarization $\boldsymbol{P}$ as induced by an applied electric field $\boldsymbol{E}$. In general, $\boldsymbol{P}$ can be written as a series in permittivity tensors

$$\boldsymbol{P}=\int \mathrm{d}^3\boldsymbol{r}\{\boldsymbol{\chi}^{(1)}(\boldsymbol{r})+\boldsymbol{\chi}^2(\boldsymbol{r})\cdot\boldsymbol{E}+\boldsymbol{\chi}^3(\boldsymbol{r})\cdot(\boldsymbol{E}\otimes\boldsymbol{E}) +\boldsymbol{\chi}^4(\boldsymbol{r})\cdot(\boldsymbol{E}\otimes\boldsymbol{E}\otimes\boldsymbol{E})+\cdots\}, \tag{2.1}$$

where $\otimes$ stands for the tensor product. Due to the *local* D_∞ or D_2 symmetries of most of the liquid crystalline phases the permanent polarization $\boldsymbol{\chi}^1$ and the third-order nonlinear susceptibility $\boldsymbol{\chi}^3$ must vanish. Hence the leading term in the expansion (2.1) is the second-rank tensor $\boldsymbol{\chi}^2(\boldsymbol{r})$. Its anisotropic part

$$Q_{\alpha\beta}(\boldsymbol{r})=\chi^2_{\alpha\beta}(\boldsymbol{r})-\frac{1}{3}\,\mathrm{Tr}[\boldsymbol{\chi}^2(\boldsymbol{r})]\,\delta_{\alpha\beta} \tag{2.2}$$

is referred to as the alignment tensor and is usually taken as a primary order parameter.

The fourth-rank tensor $\boldsymbol{\chi}^4(\boldsymbol{r})$ of components $\chi^4_{\alpha\beta\gamma\delta}(\boldsymbol{r})$ is an example of a leading secondary order parameter. In the phenomenological description of liquid crystals $\boldsymbol{\chi}^4(\boldsymbol{r})$ usually is disregarded. But for the cubic blue phases such a procedure seems questionable. Experiments of Pieranski *et al.* [11], aligning BPI and BPII crystals by an electric field, have shown that the spatially averaged nonlinear dielectric tensor $\boldsymbol{B}$, defined as

$$\boldsymbol{B}=\int d^3\boldsymbol{r}\boldsymbol{\chi}^4(\boldsymbol{r}),$$

is responsible for the orientation process. The tensor $\boldsymbol{B}$ is the $\boldsymbol{k}=\boldsymbol{0}$ Fourier component of the field $\boldsymbol{\chi}^4(\boldsymbol{r})$. The norm of $\boldsymbol{B}$ was found about 10^5 times larger than for ordinary nematics. Thus one may conclude that $\boldsymbol{B}$ must be present in the free energy expansion for the blue phases, at least when the external electric field is nonzero. It can be divided into SO(3) irreducible tensors $\boldsymbol{B}^{(L)}$ of components $B^{(L)}_{\alpha\beta\gamma\delta}$ with momenta $L=0$, 2, and 4. Since the $L=0$ part describes the SO(3) symmetric reference state and the $L=2$ part is absent in the cubic blue phases, only the $L=4$ hexadecupole part $\boldsymbol{B}^{(4)}$ of the order parameter $\boldsymbol{B}$ is relevant.

Now we expand the free energy density in terms of the two order parameters, namely, $Q_{\alpha\beta}(\boldsymbol{r})$ and $B^{(4)}_{\alpha\beta\gamma\delta}$. The expansion falls into three parts

$$\mathcal{F}=\mathcal{F}_{\mathrm{LGdG}}[\boldsymbol{Q},\partial\boldsymbol{Q}]+F_{\mathrm{coupl}}[\boldsymbol{Q},\boldsymbol{B}^{(4)}]+\mathcal{F}_{\mathrm{bond}}[\boldsymbol{B}^{(4)}]. \tag{2.3}$$

The first part represents the well known de Gennes free energy, which is composed of elastic and bulk terms in $Q_{\alpha\beta}(\boldsymbol{r})$, [1,13]

$$\mathcal{F}_{\mathrm{LGdG}}[\boldsymbol{Q}(\boldsymbol{r})]=\mathcal{F}_{\mathrm{elastic}}[\boldsymbol{Q}(\boldsymbol{r}),\partial\boldsymbol{Q}(\boldsymbol{r})]+\mathcal{F}_{\mathrm{bulk}}[\boldsymbol{Q}(\boldsymbol{r})]. \tag{2.4}$$

In terms of dimensionless units introduced by Grebel *et al.* [2] these read

$$\mathcal{F}_{\mathrm{elastic}}[\boldsymbol{Q}(\boldsymbol{r}),\boldsymbol{\partial Q}(\boldsymbol{r})]=v^{-1}\int d^3\boldsymbol{r}\left\{\frac{1}{4}\kappa^2[\epsilon_{imn}Q_{nj,m}-Q_{ij}]^2+\rho[Q_{ij,j}]^2\right\}, \tag{2.5}$$

$$\mathcal{F}_{\mathrm{bulk}}[\boldsymbol{Q}(\boldsymbol{r})]=\mathcal{F}_2+\mathcal{F}_3+\mathcal{F}_4, \tag{2.6}$$

where

$$\mathcal{F}_2=v^{-1}\tau\int d^3\boldsymbol{r}\,\mathrm{Tr}\mathbf{Q}^2,\quad \mathcal{F}_3=-\sqrt{6}v^{-1}\int d^3\boldsymbol{r}\,\mathrm{Tr}\mathbf{Q}^3,$$

$$\mathcal{F}_4=v^{-1}\int d^3\boldsymbol{r}\,\mathrm{Tr}(\boldsymbol{Q}^2)^2. \tag{2.7}$$

Here κ is the chirality parameter, t the standard reduced temperature of Landau theory, $\tau=\frac{1}{4}(t-\kappa^2)$ the renormalized reduced temperature, ρ the ratio of elastic constants, and v the volume.

The global minimization of (2.4) is very difficult and still unsolved, due to the chiral term in (2.5), which makes the gradient and the bulk free energies favor different structures [1]. Locally preferred configurations cannot be extended globally due to the presence of topological restrictions, the effect being known as *frustration*. The cubic blue phases appear as compromise structures [1].

The second term in (2.3), denoted $F_{\mathrm{coupl}}[\boldsymbol{Q},\boldsymbol{B}^{(4)}]$, describes the coupling between the order parameters. To lowest order in $\boldsymbol{Q}$ and $\boldsymbol{B}^{(4)}$ it involves only one coupling constant λ [4],

$$\mathcal{F}_{\mathrm{coupl}}=-\frac{\lambda}{3}\mathrm{B}^{(4)}_{\alpha\,\beta\,\gamma\,\delta}\int d^3\boldsymbol{r}[Q_{\alpha\beta}(\boldsymbol{r})Q_{\gamma\delta}(\boldsymbol{r})+Q_{\alpha\gamma}(\boldsymbol{r})Q_{\beta\delta}(\boldsymbol{r})+Q_{\alpha\delta}(\boldsymbol{r})Q_{\gamma\beta}(\boldsymbol{r})]. \tag{2.8}$$

The third term $\mathcal{F}_{\mathrm{bond}}$ is an arbitrary stable and SO(3) symmetric polynomial in the components of $\boldsymbol{B}^{(4)}$. Its precise form, however, is irrelevant in our analysis of the electrostriction tensor. The simplest expansion for $\mathcal{F}_{\mathrm{bond}}$ has been analysed by Jarić [14].

A global minimization of the extended free energy (2.3) recovers the BPI and the BPII space group structures found

earlier within de Gennes's theory (2.4) [4]. Furthermore, the relative orientation of the $\boldsymbol{B}^{(4)}$ and $\boldsymbol{Q}(\boldsymbol{r})$ fields (Goldstone mode), which is exclusively determined by a minimization of the coupling term (2.8), can be fixed along the [100] direction. This result is in line with the experiments of Pierański *et al.* [11].

Finally, the model (2.3) predicts a structure with cubic symmetry with $\boldsymbol{B}^{(4)} \neq \boldsymbol{0}$ and $\boldsymbol{Q}(\boldsymbol{x}) \equiv \boldsymbol{0}$, which can be made stable in that place of the phase diagram where BPIII is localized. The proposal that the model (2.3) correctly describes BPIII leads to the question whether it also explains the anomalous electrostriction of BPI. We shall clarify this issue here. All the calculations are carried out within the model of rigid helices where the deformation of the secondary order parameter $\boldsymbol{B}^{(4)}$ is disregarded. Due to this approximation the $\mathcal{F}_{\text{bond}}$ part of the free energy becomes irrelevant and we are effectively left with the coupling term (2.8).

A. Space group induced parametrization of $Q_{\alpha\beta}(\boldsymbol{r})$

Since we shall deal with periodic structures it is convenient to expand $\boldsymbol{Q}(\boldsymbol{r})$ into plane waves of definite helicity. The expansion reads

$$\boldsymbol{Q}(\boldsymbol{r}) = \sum_{*\boldsymbol{k}} \frac{1}{\sqrt{N_{*\boldsymbol{k}}}} \left\{ \sum_{\boldsymbol{k} \in *\boldsymbol{k}} \boldsymbol{Q}(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \right\}, \tag{2.9}$$

where

$$\boldsymbol{Q}(\boldsymbol{k}) = \frac{1}{V} \int \boldsymbol{Q}(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{2.10}$$

Here the wave vectors $\boldsymbol{k}$ are taken from the reciprocal lattice of a space group $\mathcal{G}$, where $*\boldsymbol{k} = \{\boldsymbol{k}' = \boldsymbol{S}\boldsymbol{k}; \{\boldsymbol{S}|\boldsymbol{t}\} \in \mathcal{G}\}$ is the star of $\boldsymbol{k}$ and $N_{*\boldsymbol{k}}$ is the number of prongs of the star $*\boldsymbol{k}$. Then the tensors $\boldsymbol{Q}(\boldsymbol{k})$ are expressed in terms of the $L=2$ spin tensors $\boldsymbol{M}_m^{(2)}(\boldsymbol{k})$

$$\boldsymbol{Q}(\boldsymbol{k}) = \sum_{m=-2}^{2} Q_m(\boldsymbol{k}) \boldsymbol{M}_m^{(2)}(\boldsymbol{k}), \tag{2.11}$$

where

$$\boldsymbol{M}_0^{(2)}(\boldsymbol{k}) = \frac{1}{\sqrt{6}} \{3\hat{\boldsymbol{k}} \otimes \hat{\boldsymbol{k}} - \boldsymbol{1}\},$$

$$\boldsymbol{M}_{\pm 1}^{(2)}(\boldsymbol{k}) = \pm \frac{1}{2} \{(\hat{\boldsymbol{v}} \pm i\hat{\boldsymbol{w}}) \otimes \hat{\boldsymbol{k}} + \hat{\boldsymbol{k}} \otimes (\hat{\boldsymbol{v}} \pm i\hat{\boldsymbol{w}})\}, \tag{2.12}$$

$$\boldsymbol{M}_{\pm 2}^{(2)}(\boldsymbol{k}) = \frac{1}{2} \{(\hat{\boldsymbol{v}} \pm i\hat{\boldsymbol{w}}) \otimes (\hat{\boldsymbol{v}} \pm i\hat{\boldsymbol{w}})\}$$

are defined with respect to an orthonormal, right-handed local coordinate system $\{\hat{\boldsymbol{v}}, \hat{\boldsymbol{w}}, \hat{\boldsymbol{k}}\}$ with $\hat{\boldsymbol{k}} = \boldsymbol{k}/|\boldsymbol{k}|$. The reality condition $\boldsymbol{Q}(\boldsymbol{r}) = [\boldsymbol{Q}(\boldsymbol{r})]^*$ additionally implies that

$$\boldsymbol{M}_m^{(2)}(-\boldsymbol{k}) = (-1)^m [\boldsymbol{M}_m^{(2)}(\boldsymbol{k})]^*. \tag{2.13}$$

Hence the complete expression for $Q_{\alpha\beta}(\boldsymbol{r})$ reads

$$\boldsymbol{Q}(\boldsymbol{r}) = \sum_{*\boldsymbol{k}} \frac{1}{\sqrt{N_{*\boldsymbol{k}}}} \left\{ \sum_{\boldsymbol{k} \in *\boldsymbol{k}} \left(\sum_{m=-2}^{2} Q_m(\boldsymbol{k}) M_m(\boldsymbol{k}) \right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \right\}. \tag{2.14}$$

A standard way of minimizing $\mathcal{F}_{\text{LGdG}}$ is to find an active representation in the expansion (2.14) first. It is achieved by minimizing the quadratic part of the free energy $\mathcal{F}_{\text{elastic}} + \mathcal{F}_2$ with respect to m [see (2.5) and (2.7)], which yields the $m = 2\ \text{sgn}(\kappa)$ helicity mode. The choice simultaneously eliminates the elastic constant ρ from further considerations [2].

B. The secondary order parameter $\boldsymbol{B}^{(4)}$

The second ingredient of the theory is the fourth-rank tensor $\boldsymbol{B}^{(4)}$. A similar tensor has been introduced by Nelson and Toner [15] to describe the melting process of atomic crystals. They assumed that due to large fluctuations of the atomic positions or unbinding of the dislocation dipoles the translational order of a crystal is destroyed, but the bonds of different atomic clusters remain oriented. In the case of BPIII, modeled in terms of $\boldsymbol{B}^{(4)}$, the situation is similar, namely, the periodic sequence of cubic unit cells is interrupted but the substructures of the cells preserve a long-range cubic alignment.

The part $\mathcal{F}_{\text{bond}}[\boldsymbol{B}^{(4)}]$ of the free energy, responsible for the residual long-range order, is a polynomial in the components of $\boldsymbol{B}^{(4)}$. Calculations show that for the $\boldsymbol{B}^{(4)}$ tensors minimizing the simplest form of $\mathcal{F}_{\text{bond}}[\boldsymbol{B}^{(4)}]$ there are only three stable point group symmetries: O_h, $D_{\infty h}$, and D_{4h} [14], adjacent to the isotropic state I. The phase diagram is dominated by the octahedral structure O_h, which is accessed through either a first-order phase transition or a multicritical continuous transition. The transition I to $D_{\infty h}$ is of first order, whereas the transition I to D_{4h} is of second order and the least probable one. Therefore, and because structures of $D_{\infty h}$ symmetry have not been detected experimentally in the blue phases, $\boldsymbol{B}^{(4)}$ is restricted to the space of O_h symmetric hexadecupole tensors:

$$\boldsymbol{B}^{(4)} = B_0 \sqrt{2 \times 5 \times 7} \left\{ \sqrt{\frac{5}{14}} [\boldsymbol{M}_4^{(4)}(\hat{\boldsymbol{n}}) + \boldsymbol{M}_{-4}^{(4)}(\hat{\boldsymbol{n}})] + \boldsymbol{M}_0^{(4)}(\hat{\boldsymbol{n}}) \right\}. \tag{2.15}$$

Here B_0 is the norm of the tensor $\boldsymbol{B}^{(4)}$ and $\boldsymbol{M}_m^{(4)}(\hat{\boldsymbol{n}})$ are spin $L=4$ orthonormal tensors represented in an orthonormal right-handed triad $\{\hat{\boldsymbol{n}}_1, \hat{\boldsymbol{n}}_2, \hat{\boldsymbol{n}}_3 = \hat{\boldsymbol{n}}\}$. The Goldstone mode, represented by the triad $\{\hat{\boldsymbol{n}}_1, \hat{\boldsymbol{n}}_2, \hat{\boldsymbol{n}}\}$, has been taken parallel to $[n00]$ directions of the O^2 and O^8 structures.

III. ELECTROSTRICTION OF CUBIC BLUE PHASES

The deformation of the cubic lattices of blue phases by an electric field depends crucially on the field strength. In a weak field, both BPI and BPII crystals are oriented with their [100] axis parallel to the field $\boldsymbol{E}$, as observed by Pierański *et al.* [11]. The authors pointed out that the nonlinear dielectric susceptibility $\boldsymbol{\chi}^{(4)}$ is responsible for the orientation of the BPI and BPII crystals. It is precisely this observable that matches the bond orientational order parameter $\boldsymbol{B}^{(4)}$.

In stronger fields, the phenomenon of electrostriction, i.e.,

the continuous deformation of the structure, occurs. In particular, BPI shows the so-called *anomalous electrostriction*. It means that the sample is dilated or compressed along the field direction, depending on the orientation of the field with respect to the crystallographic axes.

Finally, with still larger fields, the blue phases may transform to noncubic blue phases (tetragonal, hexagonal two-dimensional, or three-dimensional), to the cholesteric phase, and also to the nematic phase [16].

A. The electrostriction tensor

Electrostriction can be viewed as a competition between elastic and electric forces that results in an equilibrium deformation of the structure. The deformation is described by the symmetric deformation tensor $\boldsymbol{\varepsilon}$:

$$\varepsilon_{ij}=\frac{1}{2}(\nabla_i v_j+\nabla_j v_i), \tag{3.1}$$

where the vector of components v_i characterizes a shift of the lattice points under the deformation. In the blue phases ε_{ij} describes a deformation of the mean molecular orientations but not a translation of the centers of mass.

Using the notation of Stark and Trebin [7], the free energy for a distorted blue phase in an external electric field $\boldsymbol{E}$ is given by

$$\mathcal{F}_{\text{distortion}}=\frac{1}{2}\boldsymbol{C}\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon})-\frac{\delta'}{8\pi}\boldsymbol{\chi}(\boldsymbol{r})\cdot(\boldsymbol{E}\otimes\boldsymbol{E}). \tag{3.2}$$

The first term represents the elastic free energy, where $\boldsymbol{C}$ is the matrix of elastic constants. The second term characterizes the electrostatic free energy, with δ' being a constant that takes into account the difference between the internal and the external electric field.

The dielectric tensor $\boldsymbol{\chi}(\boldsymbol{r})$ of the distorted structure can also be expanded with respect to the deformation tensor $\boldsymbol{\varepsilon}$. To lowest order in $\boldsymbol{\varepsilon}$ and $\boldsymbol{E}$ it reads

$$\boldsymbol{\chi}=\chi_0\mathbf{1}+\boldsymbol{b}\boldsymbol{\varepsilon}+\boldsymbol{\chi}^4(\boldsymbol{E}\otimes\boldsymbol{E}), \tag{3.3}$$

where χ_0 is the isotropic term, $\boldsymbol{b}$ the elastooptic tensor, and $\boldsymbol{\chi}^4$ the nonlinear dielectric susceptibility defined by Eq. (2.1).

The equilibrium value of the deformation tensor $\boldsymbol{\varepsilon}$ is found by minimizing $\mathcal{F}_{\text{distorsion}}$, Eq. (3.2), for a given value of $\boldsymbol{E}$. It yields

$$\frac{\partial\mathcal{F}_{\text{distortion}}}{\partial\boldsymbol{\varepsilon}}=0=\boldsymbol{C}\boldsymbol{\varepsilon}-\frac{\delta'}{8\pi}\boldsymbol{b}^t(\boldsymbol{E}\otimes\boldsymbol{E}), \tag{3.4}$$

where

$$\boldsymbol{\varepsilon}=\boldsymbol{R}(\boldsymbol{E}\otimes\boldsymbol{E}), \tag{3.5}$$

with

$$\boldsymbol{R}=\frac{\delta'}{8\pi}\boldsymbol{s}\boldsymbol{b}^t. \tag{3.6}$$

Here $\boldsymbol{s}$ is the matrix inverse to the matrix of elastic constants and $\boldsymbol{R}$ is the electrostriction tensor.

As the free energy is a scalar, it has to be invariant under operations of the point group G. In the case of the cubic blue phases, the symmetry induces the following restrictions on the tensors $\boldsymbol{C}$ and $\boldsymbol{b}$ [17]: (i) they are symmetric in both the first and the second pair of indices, (ii) they are invariant under the exchange of the indices within a pair, and (iii) for cubic symmetry the number of independent components of $\boldsymbol{C}$ and $\boldsymbol{b}$ is reduced to 3. Using the Voigt notation the tensor of elastic constants can be written as

$$\boldsymbol{C}=\begin{pmatrix} C_1 & C_2 & C_2 & 0 & 0 & 0\\ C_2 & C_1 & C_2 & 0 & 0 & 0\\ C_2 & C_2 & C_1 & 0 & 0 & 0\\ 0 & 0 & 0 & C_3 & 0 & 0\\ 0 & 0 & 0 & 0 & C_3 & 0\\ 0 & 0 & 0 & 0 & 0 & C_3 \end{pmatrix},$$

where $C_1=C_{1111}$, $C_2=C_{1122}$, and $C_3=C_{1212}$. Consequently, the electrostriction tensor $\boldsymbol{R}$ also has only three independent components: $R_1=R_{1111}$, $R_2=R_{1122}$, and $R_3=2R_{2323}$.

B. Calculation of the free energy of distortion

Let us assume that $\boldsymbol{r}$ is a vector describing the position of the lattice points before the deformation. Then, to lowest order, the position $\tilde{\boldsymbol{r}}$ of the distorted structure is

$$\tilde{\boldsymbol{r}}=(\mathbf{1}+\boldsymbol{\varepsilon})\boldsymbol{r}. \tag{3.7}$$

The wave vectors $\tilde{\boldsymbol{k}}$ of the distorted reciprocal lattice transform inversely

$$\tilde{\boldsymbol{k}}=(\mathbf{1}+\boldsymbol{\varepsilon})^{-1}\boldsymbol{k}\approx(\mathbf{1}-\boldsymbol{\varepsilon})\boldsymbol{k}. \tag{3.8}$$

The deformation of the $\boldsymbol{k}$ vectors rotates the tensors $\boldsymbol{M}_2^{(2)}(\boldsymbol{k})$. Additionally, $\boldsymbol{Q}(\boldsymbol{k})$ acquires the homogeneous part $\boldsymbol{b}\boldsymbol{\varepsilon}$ [see Eq. (3.3)]. Such a term is forbidden in the undistorted structure due to symmetry. Under the assumptions of the model of rigid helices, the scalar amplitudes $Q_2(\boldsymbol{k})$ do not change. In summary, the order parameter $\boldsymbol{Q}(\boldsymbol{r})$ changes under a deformation in the following way [7]:

$$\boldsymbol{Q}(\boldsymbol{r})=\sum_{\boldsymbol{k}} Q_2(\boldsymbol{k})\boldsymbol{M}_2^{(2)}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\xrightarrow{\boldsymbol{\varepsilon}}\tilde{\boldsymbol{Q}}(\boldsymbol{r})$$

$$=\boldsymbol{b}\boldsymbol{\varepsilon}+\sum_{\boldsymbol{k}} Q_2(\boldsymbol{k})\boldsymbol{M}_2^{(2)}(\tilde{\boldsymbol{k}})e^{i\tilde{\boldsymbol{k}}\cdot\boldsymbol{r}}.$$

Again the distorted tensors $\boldsymbol{M}_2^{(2)}(\tilde{\boldsymbol{k}})$ can be expanded with respect to the deformation tensor $\boldsymbol{\varepsilon}$. The corresponding formulae have been derived by Stark and Trebin [7].

The assumptions discussed above imply that the small change of the secondary order parameter under deformation $\boldsymbol{B}^{(4)}$ can be disregarded, i.e.,

$$\boldsymbol{B}^{(4)}\xrightarrow{\boldsymbol{\varepsilon}}\tilde{\boldsymbol{B}}^{(4)}=\boldsymbol{B}^{(4)}.$$

The excess free energy resulting from the distortion of the cubic ground state reads

$$\Delta\mathcal{F}=\Delta\mathcal{F}_{\boldsymbol{Q}}+\Delta\mathcal{F}_{\mathrm{coupl}}, \tag{3.9}$$

where

$$\Delta\mathcal{F}_{\boldsymbol{Q}}=\mathcal{F}_{\mathrm{LGdG}}[\widetilde{\boldsymbol{Q}}]-\mathcal{F}_{\mathrm{LGdG}}[\boldsymbol{Q}], \tag{3.10}$$

$$\Delta\mathcal{F}_{\mathrm{coupl}}=\mathcal{F}_{\mathrm{coupl}}[\widetilde{\boldsymbol{Q}}]-\mathcal{F}_{\mathrm{coupl}}[\boldsymbol{Q}]. \tag{3.11}$$

The calculation of $\Delta\mathcal{F}_{\boldsymbol{Q}}$ is divided into three steps: (i) the contribution due to the quadratic part,

$$\mathcal{F}_{\mathrm{elastic}}[\widetilde{\boldsymbol{Q}},\partial\widetilde{\boldsymbol{Q}}]+\mathcal{F}_2[\widetilde{\boldsymbol{Q}}]-\mathcal{F}_{\mathrm{elastic}}[\boldsymbol{Q},\partial\boldsymbol{Q}]-\mathcal{F}_2[\boldsymbol{Q}]$$
$$=\frac{1}{2}\boldsymbol{C}^{(2)}\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon})+\frac{t}{4}\boldsymbol{b}^t\boldsymbol{b}\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon}); \tag{3.12}$$

(ii) the contribution due to the cubic part,

$$\mathcal{F}_3[\widetilde{\boldsymbol{Q}}]-\mathcal{F}_3[\boldsymbol{Q}]=-\sqrt{6}(\boldsymbol{C}_3+\boldsymbol{b}\boldsymbol{v}_3)\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon}); \tag{3.13}$$

and (iii) the contribution due to the quartic part,

$$\mathcal{F}_4[\widetilde{\boldsymbol{Q}}]-\mathcal{F}_4[\boldsymbol{Q}]=(\boldsymbol{C}_4+\boldsymbol{b}\boldsymbol{v}_4+4\boldsymbol{b}^t\boldsymbol{w}\boldsymbol{b}+2\mu\boldsymbol{b}^t\boldsymbol{b})\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon}). \tag{3.14}$$

Finally, the contribution due to the coupling term reads

$$\mathcal{F}_{\mathrm{coupl}}[\widetilde{\boldsymbol{Q}},\boldsymbol{B}^{(4)}]-\mathcal{F}_{\mathrm{coupl}}[\boldsymbol{Q},\boldsymbol{B}^{(4)}]$$
$$=-\lambda B_0(\boldsymbol{C}_{\mathrm{coupl}}+\boldsymbol{b}^t\boldsymbol{B}^{(4)}\boldsymbol{b})\cdot(\boldsymbol{\varepsilon}\otimes\boldsymbol{\varepsilon}). \tag{3.15}$$

In later calculations λB_0 is treated as a single free parameter of the theory.

Adding up all the terms (3.12)–(3.15), the excess free energy can now be written as

$$\Delta\mathcal{F}=\frac{1}{2}C_{IK}\varepsilon_I\varepsilon_K, \tag{3.16}$$

where

$$C_{IK}=C^0_{IK}-\delta(M)b_{MI}v_{MK}+\left(\frac{t}{2}+4\mu\right)\delta(M)b_{MI}b_{MK}$$
$$+\delta(M)\delta(R)b_{MI}w_{MR}b_{RK}, \tag{3.17}$$

$$C^0_{IK}=[\boldsymbol{C}_2-2\sqrt{6}\boldsymbol{C}_3+2\boldsymbol{C}_4-2a\boldsymbol{C}_{\mathrm{coupl}}]_{IK}, \tag{3.18}$$

$$-v_{IK}=[-2\sqrt{6}\boldsymbol{v}_3+2\boldsymbol{v}_4]_{IK}, \tag{3.19}$$

$$w_{IK}=[8\boldsymbol{w}-2a\boldsymbol{B}^{(4)}]_{IK}, \tag{3.20}$$

with

$$\delta(M)=\begin{cases}1 & \text{if } M=1,2,3\\ 2 & \text{if } M=4,5,6.\end{cases} \tag{3.21}$$

(Indices written in capital letters imply that Voit notation is used. The Einstein summation convention over repeated indices is to be understood.) Then, the elastooptic tensor $\boldsymbol{b}$ is determined by minimization of the free energy with respect to b_{ST}. Finally, the independent components of the electrostriction tensor are

$$R_1=\frac{\delta'}{8\pi}\frac{b_1}{C_1-C_2}=-2R_2, \tag{3.22}$$

and

$$R_3=\frac{\delta'}{8\pi}\frac{b_3}{C_3}. \tag{3.23}$$

IV. RESULTS

In the preceding section we derived the electrostriction tensor by studying a perturbation of the cubic ground states of BPI and BPII. Hence the numerical values of this tensor depend on the order parameters $\boldsymbol{Q}$ and $\boldsymbol{B}^{(4)}$ that minimize the free energy (2.3) of the unperturbed states. Under the approximation of rigid helices the minimization considerably simplifies as the purely bond order part does not enter directly the electrostriction tensor calculations. Consequently, it is sufficient to minimize the de Gennes part (2.4) of the total free energy (2.3) and the coupling part (2.8) and treat the product λB_0 as a free parameter.

Being aware of the fact that the free energy (2.4) does not reproduce the relative stability of BPI and BPII structures, we used a minimization procedure consisting of two parts. First of all, only the *relative* stability of BPI and the isotropic phase was considered. Second, the same minimization was carried out by assuming that only BPII and the isotropic phase are present. Thus we searched for the regions on the phase diagram where the particular cubic blue phase had lower free energy than the isotropic phase. More specifically, for fixed values of the parameters κ, λB_0, and of the temperature we found the values of the scalar amplitudes $Q_2(\boldsymbol{k})$ corresponding to a minimum of the free energy up to three stars of symmetry allowed $\boldsymbol{k}$ vectors. Taking into account that the amplitude of the fourth star is negligible, this makes our calculations consistent with those of Grebel *et al.* [2]. The temperature interval was scanned from $t=-4$ up to the transition temperature between BPI (BPII) and the isotropic phase. For the amplitudes $Q_2(\boldsymbol{k})$ found for BPI and BPII, the numerical values of the independent components (3.22) and (3.23) of the electrostrition tensor were tabulated.

We also compared our results with those of Stark and Trebin [7] by assuming that $\lambda B_0=0$. The ratio R_1/R_3 calculated here is larger than in [7] by an amount of 10% (small chiralities) to 30% (large chiralities). In the work of Stark and Trebin the summations over $\boldsymbol{k}$ vectors of various stars were simplified with the help of group theory and, up to third order [Eq. (3.13)], were done exactly. However, the fourth-order contributions [Eq. (3.14)], due to extremely large number of terms, have only been found approximately. We succeeded in deriving exact formulas for this case by using MAPLE and FORTRAN programs. It should be mentioned that, as a test of a proper space group parametrization of the ground states, the free energy of the O^2 and the O^8 structures calculated earlier by Grebel *et al.* [2] has been recovered.

We have extended the results to the case of nonvanishing coupling λB_0 and have determined the temperature depen-

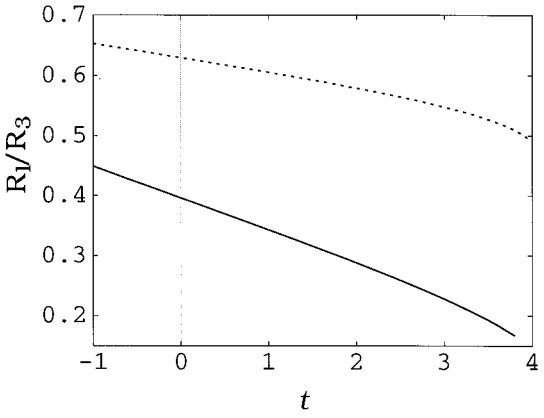

FIG. 1. Temperature dependence of the ratio R_1/R_3 for $\lambda B_0=0.0$ and $\kappa=1.8$. Here and in the following figures the solid line represents the behavior of O^2, whereas the dashed line belongs to O^8.

dence of the ratio R_1/R_3. The results are given in Figs. 1–4. In Figs. 1–3, the values of the parameters κ and λB_0 are fixed and the ratio R_1/R_3 is calculated for each temperature separately.

Note that for $\lambda B_0=0$ (Fig. 1) all the values of the ratios R_1/R_3 are positive and less than unity, indicating that the experimentally observed behavior of electrostriction of BPI cannot be explained. We tested the influence of the increasing coupling strength λB_0 on the electrostriction (see Fig. 2). Here the ratio R_1/R_3 becomes negative for BPI, while it remains positive for BPII. This is the case of the *anomalous electrostriction*. When still increasing the coupling strength, we arrive at the situation presented in Fig. 3, where R_1/R_3 can be negative for both structures.

All the results are summarized in Fig. 4. It shows the areas in $(\lambda B_0,\kappa)$ plane, where the anomalous electrostriction can occur irrespectively of the value of the temperature. Five regions can be distinguished. In the first area, denoted $\boldsymbol{O}^8$, only BPI behaves anomalously. Then follows the area $(\boldsymbol{O}^8+\boldsymbol{O}^2)$, where R_1/R_3 is negative for both structures. For still higher coupling strength only BPII behaves anomalously

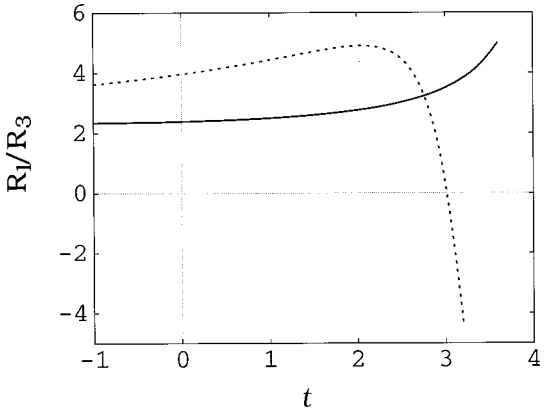

FIG. 2. Temperature dependence of the ratio R_1/R_3 for $\lambda B_0=0.3$ and $\kappa=1.6$.

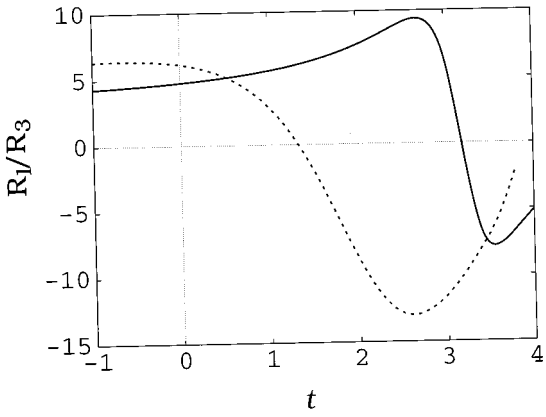

FIG. 3. Temperature dependence of the ratio R_1/R_3 for $\lambda B_0=0.4$ and $\kappa=1.6$.

$(\boldsymbol{O}^2)$. In the remaining two areas, the ratio R_1/R_3 is positive for BPI and BPII.

However, as it has been recently shown by Englert, Longa, and Trebin [18], for higher values of the coupling parameter λB_0, BPI may vanish from the phase diagram. So it seems reasonable to consider only the weak couplings.

V. SUMMARY

We have studied an extended Landau–Ginzburg–de Gennes theory to search for an explanation of the anomalous electrostriction of BPI. Exact calculations have been carried out within the approximation of *rigid helices*, extending earlier work by Stark and Trebin [7]. These studies allow us to test the effect of coupling (2.8) between the bond orientational tensor $\boldsymbol{B}^{(4)}$ and the alignment tensor $\boldsymbol{Q}(\boldsymbol{r})$ on the electrostriction tensor $\boldsymbol{R}$.

The results of Sec. IV show that the anomalous electro-

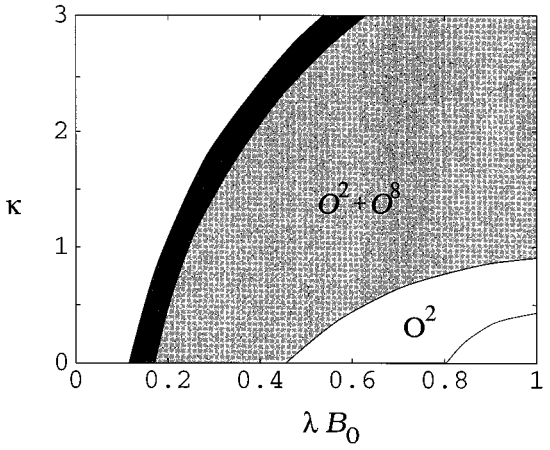

FIG. 4. Range of the coupling λB_0 where the anomalous electrostriction can occur. Five regions can be distinguished. In the first area, denoted $\boldsymbol{O}^8$, only BPI behaves anomalously. Then follows the area $(\boldsymbol{O}^8+\boldsymbol{O}^2)$, where R_1/R_3 is negative for both structures. For still higher coupling strength only BPII behaves anomalously $(\boldsymbol{O}^2)$. In the remaining two areas, the ratio R_1/R_3 is positive for BPI and BPII.

striction of the BPI is explained with the help of the bond-order tensor. However, for certain values of the parameter λB_0, such an anomalous behavior may also be induced in the BPII phase, which is not observed experimentally.

The results show that the bond orientational order parameter $\boldsymbol{B}^{(4)}$ is a relevant parameter, at least in the description of the cubic blue phases. The values of the coupling constant λB_0 for which the anomalous behavior is induced in BPI but not in the BPII give hints regarding models proposed for the structure of the blue fog.

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