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## Liquid Crystals

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# Cubic bond orientational order in the liquid crystalline blue phases

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A thorough numerical analysis of a recently proposed cubic bond orientational model for Blue Phase III (Longa, L., and Trebin, H.-R., 1993, *Phys. Rev. Lett.*, **71**, 2757) is presented. In addition to the standard quadrupolar tensor field  $Q_{\alpha\beta}(\mathbf{r})$ , describing the cubic space groups of BPI and BPII, a spatially constant fourth-rank hexadecupolar tensor  $B_{\alpha\beta\gamma\delta}^4$  of cubic point group symmetry is used to describe a cubic bond orientational order. While in BPI and BPII both order parameters are present, in BPIII only the hexadecupolar tensor is non-zero. Hence, BPIII is viewed as a phase of long-range cubic order. Within this model distinct phase diagrams are computed up to four stars of  $\mathbf{k}$ -vectors, the elements of a star being related by the point group symmetry operations. In particular, it is possible to account for some of the details found experimentally, such as the dominance of BPI over BPII for high chiralities. If, however, the artificial body centred cubic structure  $O^5$  is being made metastable, then BPI also vanishes from the phase diagram.

## 1. Introduction

Blue Phases of chiral liquid crystals, also known as BPI, BPII and BPIII, have puzzled research for more than a century now [1]. While it seems most probable that BPI and BPII have periodicities of a body-centred cubic structure with the space group symmetry  $O^8(I4_132)$  and of a simple cubic structure with the space group symmetry  $O^2(P4_232)$ , respectively, the structure of BPIII is still a matter of intensive theoretical and experimental studies. Though being selective to the handedness of circularly polarized light in reflection like the other two Blue Phases [1], it does not exhibit sharp Bragg peaks, but rather a wide reflection band [2] typical of an amorphous system. Most probably it also does not possess long range periodic order, a conjecture which is supported by Grandjean–Cano measurements [3].

For moderate chiralities all the phase transitions between the Blue Phases are first order, with the transition enthalpy smaller by two orders of magnitude than that between the isotropic phase (I) and BPIII. For highly chiral liquid crystalline compounds, the transition enthalpy I–BPIII decreases with increasing chirality [4] and may even vanish at a certain limiting chirality [5]

suggesting the presence of an intermediate critical or tricritical point. These observations seem to indicate that, at least, short range order must be similar in all BPs.

Though critical fluctuations supporting the existence of the (tri-)critical point between BPIII and I have not been observed so far, the decrease of the latent heat down to a non-detectable value [4,5] puts severe restrictions on a hypothetical structure of BPIII. Two possibilities seem most probable. The first one is that BPIII and I phases are of the same macroscopic symmetry and approach a common critical point at high chiralities; this scenario seems to be favoured by current experiments [4,5]. The second possibility is that BPIII and I phases are of different symmetry with a high-chirality tricritical point. It could serve as a very interesting alternative to the first case and is not excluded at experimental level.

Modelling the structures of Blue Phases has a long history [1,6–11]. In general the cubic structures of BPI and BPII emerge correctly from the calculations [12]. Also the order of the phase transitions between I, Ch, BPI and BPII is found to agree with experiment. However, neither of the proposed mean field calculations explains the structure of BPIII. The cubic  $O^5$  structure theoretically found in the phase diagram, where normally BPIII is stabilized, has never been observed experiment-

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ally. Also the other features of the experimental phase diagrams such as, for example, a restricted stability domain of BPII, remain unexplained. On the contrary, the theoretical phase diagram is *dominated* by BPII. Both a typical experimental phase diagram [3] and the best theoretical phase diagram found to date [12] are shown in figure 1.

Among the proposed models aiming to solve the BPIII puzzle, some are of particular interest as they indicate that BPIII could be a new form of liquid state not seen before. One of them is an *icosahedral model* [6, 7], which assumes that BPIII is a thermodynamically stable icosahedral liquid possessing a quasi-periodic icosahedral symmetry of the orientational degrees of freedom. Unfortunately, the calculations show that the icosahedral structure cannot account for a (tri-)critical point. If the icosahedral liquid were a stable phase, the phase transition from I to this structure would always be first order. At a theoretical level, to get an icosahedral structure as (at least) a metastable state is however not excluded. This possibility seems inherent to the de Gennes–Ginzburg–Landau description of chiral liquid crystals [7, 13].

To summarize, mean-field theories based solely on the alignment tensor as an order parameter have not been successful in their goal to obtain a *generic* phase diagram with a correct identification of BPIII. This failure gave a motivation for seeking another route to explain its structure. In this paper we shall extend the standard de Gennes–Ginzburg–Landau theory to show that some of the features of the experimentally observed phase diagrams can be accounted for theoretically using the concept of ‘bond order’. A possible interpretation of the structure of the BPIII will be given. More specifically, in a recent paper [9] we argued that the correct solution to the problem of the BPIII structure cannot be obtained without taking into account fluctuations of the orienta-

tional order on a scale exceeding, say, the pitch and that of chirality induced correlations for smaller distances. The presence of strong fluctuations is observed in BPI and BPII in the form of incoherent light scattering which breaks geometrical selection rules for Bragg peaks [1].

The proposed scenario [9–11] (to be discussed later) implied that, at least, two possibilities for the structure of BPIII could be envisaged. The first possibility yields a family of *isotropic models* [1, 10, 11] which view BPIII as a new type of ‘amorphous’ liquid differing from the ordinary isotropic liquid by short-range correlations. Within these models a critical point between I and BPIII is not excluded [10, 11]. Detailed calculations will be published elsewhere.

The second possibility is known as a *cubic bond orientational model* [8–10]. This model assumes that due to strong fluctuations of the tensor field  $Q_{\alpha\beta}(\mathbf{r})$ , the cubic space group symmetries of ordinary cubic blue phase superlattices become reduced to their common octahedral factor group  $O(432) \equiv O_h$ . Diffraction maxima should still be observed, but there are no periodic planes to produce coherent Bragg diffraction, which generally agrees with experiments. Such a concept has long ago been envisaged by Nelson and Toner for atomic crystals [14] but has never been reported in three dimensions. The cubic bond model could account for a tricritical BPIII–I phase transition [15].

The phase diagrams are usually calculated by minimization of the free energy functional of the order parameter field in Fourier space. The expansion of the field in Fourier components is limited to a finite number of sets of wave vectors. The elements of a set are transformed mutually by the operations of the point group and have the same lengths. Elements of different sets generally differ in length. We denote these sets by ‘stars’ or ‘shells’. They are characterized by representatives such as, e.g. [100] and [110] for  $O^2$ .

Two star calculations of the phase diagrams within an extended de Gennes–Landau–Ginzburg free energy [9] indicated that the bcc structure  $O^5$  ( $P432$ ) could be removed from the phase diagram, and the bond orientational ordered phase could be stabilized in the regime of high temperatures. As the calculations of the diagram in figure 1 [12] revealed a strong sensitivity to details of parametrization of the tensor field, it is a purpose of this paper to generalize the previous analysis to four star calculations. These will make the analysis consistent with the calculations of Grebel *et al.* [12].

After introducing the de Gennes–Wilson–Ginzburg–Landau theory in §2 we shall be concerned in §3 with the extended free energy which accounts for bond orientational order. In §4 we provide a detailed, four star

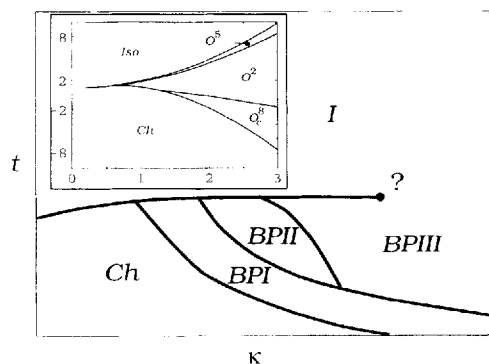


Figure 1. Typical experimental phase diagram as found by Yang and Crooker. The best theoretical diagram of Grebel *et al.* [12] is also shown as the inset.

analysis of the phase diagrams for Blue Phases that follow from such a theory.

## 2. De Gennes–Ginzburg–Landau free energy

There are different levels of description for phase transitions between liquid crystalline phases. At a microscopic level with a characteristic length scale of, say, 40 Å the properties of the system are calculated using statistical mechanics. The starting point of such calculations lies in interactions between the molecules. At a mesoscopic level with a characteristic length of 400 Å, the concept of order parameters is introduced and the observables are calculated using statistical field theory. Finally, at a macroscopic level of resolution of 4000 Å, the mesoscopic order parameters are often used as input. The mesoscopic and macroscopic scales allow one to explain the universal behaviour of the systems, independent of details of microscopic interactions. Clearly, all three levels of description are closely correlated.

For the cholesteric phase and for the Blue Phases of chiral liquid crystal materials, the characteristic dimension associated with the structure is of the order of 4000 Å. Consequently, the mesoscopic level is an appropriate starting point of the description. The order parameters can be identified with the help of macroscopic response functions of the bulk material [16] or by referring to the angular distribution function  $f_r(\theta, \phi)$  of orientational degrees of freedom and by exploiting its symmetry properties. In the latter case coefficients of the expansion of  $f_r(\theta, \phi)$  in powers of the directional unit vector  $\hat{\nu} = (\cos \phi \sin \theta, \sin \phi \sin \theta, \cos \theta)$  serve as order parameters:

$$f_r(\theta, \phi) = f_r(\hat{\nu}) = \frac{1}{4\pi} [\mathbf{N}(\mathbf{r}) + 3\mathbf{D}(\mathbf{r}) \cdot \hat{\nu} + 5\mathbf{Q}(\mathbf{r}) : (\hat{\nu} \otimes \hat{\nu}) + 7\mathbf{M}(\mathbf{r}) : (\hat{\nu} \otimes \hat{\nu} \otimes \hat{\nu}) + 9\mathbf{B}^4(\mathbf{r}) : (\hat{\nu} \otimes \hat{\nu} \otimes \hat{\nu} \otimes \hat{\nu}) + \dots]. \quad (1)$$

Here  $\mathbf{N}, \mathbf{D}, \mathbf{Q}, \dots$  are the irreducible tensors of momenta  $L=0, 1, 2, \dots$ , respectively. For local  $SO(3)$ -,  $D_\infty$ - or  $D_2$  symmetries, which are relevant for the systems studied, the tensors of odd  $L$  vanish. The monopole momentum ( $N$ ) normalizes the distribution  $f_r$ . Thus the lowest order non-trivial field which can be identified with the primary order parameter of liquid crystals is the symmetric and traceless quadrupolar tensor field  $\mathbf{Q}(\mathbf{r})$ . As already indicated before,  $\mathbf{Q}(\mathbf{r})$  can be associated with the anisotropic part of the diamagnetic, or dielectric linear susceptibility. The position dependence of  $\mathbf{Q}$  takes into account a possibility of non-uniform configurations of the orientational degrees of freedom. Later we shall introduce a secondary, position-independent tensor order parameter of rank four ( $\mathbf{B}^4$ ) which can be interpreted as the

hexadecupolar, non-linear part of the dielectric permittivity.

The degeneracy of the tensor  $\mathbf{Q}(\mathbf{r})$  is directly related to the local symmetry of liquid crystals. For example the local,  $SO(3)$ -symmetric (isotropic) state corresponds to the case when three eigenvalues of  $\mathbf{Q}(\mathbf{r})$  are equal. Due to the condition of vanishing traces, this symmetry yields  $\mathbf{Q}(\mathbf{r}) \equiv 0$ . For the local,  $D_\infty$ -symmetric (uniaxial) configuration, two out of the three eigenvalues of  $\mathbf{Q}(\mathbf{r})$  are equal. In the case of the general,  $D_2$ -symmetric (biaxial) structure,  $\mathbf{Q}(\mathbf{r})$  has three different eigenvalues.

In the statistical field theory the suitable quantity describing equilibrium structures is the free energy  $\mathcal{F}$ . It is defined as a Feynman integral of a Ginzburg–Landau functional  $F_{\text{deGL}}[\mathbf{Q}(\mathbf{r}), \partial\mathbf{Q}(\mathbf{r})]$  over all fields  $\mathbf{Q}(\mathbf{r})$

$$\mathcal{F} = -k_B T \ln \int \mathcal{D}\mathbf{Q}(\mathbf{r}) \exp \left\{ \frac{-F_{\text{deGL}}[\mathbf{Q}(\mathbf{r}), \partial\mathbf{Q}(\mathbf{r})]}{k_B T} \right\}. \quad (2)$$

The only restriction on  $F_{\text{deGL}}$  is that it must be (a)  $SO(3)$ -symmetric and (b) stable against an unlimited growth of both  $\mathbf{Q}(\mathbf{r})$  and  $\partial\mathbf{Q}(\mathbf{r})$ . The path integral  $\int \mathcal{D}\mathbf{Q}(\mathbf{r})$  is defined by cutting the three-dimensional volume occupied by the system into small cubes and performing integration over five fields  $Q_{\alpha\beta}$  at each point.

De Gennes was the first to formulate the Ginzburg–Landau free-energy functional  $F_{\text{deGL}}$  of liquid crystals as an expansion in terms of  $\mathbf{Q}(\mathbf{r})$  and its derivatives  $Q_{\alpha\beta,\gamma}$ . Except for the chiral term, the original expansion (which we shall refer to as de Gennes–Ginzburg–Landau theory) reads [17]

$$\begin{aligned} F_{\text{deGL}} &= F_2 + F_3 + F_4 \\ F_2 &= \frac{1}{2v} \int d^3\mathbf{r} (a \text{Tr} \mathbf{Q}^2 + c_1 (\nabla \otimes \mathbf{Q}) : (\nabla \otimes \mathbf{Q}) \\ &\quad + c_2 (\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q}) - 2d (\nabla \times \mathbf{Q}) : \mathbf{Q}) \quad (3) \\ F_3 &= -\frac{\beta}{v} \int d^3\mathbf{r} \text{Tr} \mathbf{Q}^3 \\ F_4 &= \frac{\gamma}{v} \int d^3\mathbf{r} (\text{Tr} \mathbf{Q}^2)^2. \end{aligned}$$

The chiral term (of coefficient  $2d$ ) in equation (3) is responsible for the formation of phases with broken chiral symmetry, e.g. cholesteric or the Blue Phases.

So far there has been little progress in understanding the physical implications of the statistical field theory (2) [1]. The major complication is the presence of the chiral term in  $F_{\text{deGL}}$ . Consequently most of the results are obtained using the mean-field approximation (MFA) to (2). The latter is usually introduced by expanding (3)

around the field  $\mathbf{Q}^G(\mathbf{r})$  that minimizes  $F_{\text{deGL}}$ . Then

$$\begin{aligned} \mathcal{F} \approx & F_{\text{deGL}}[\mathbf{Q}^G, \delta\mathbf{Q}^G] - \beta^{-1} \ln \int D\mathbf{Q}(\mathbf{r}) \\ & \times \exp \left[ -\frac{\beta}{2} \left\langle [\mathbf{Q}(\mathbf{r}_1) - \mathbf{Q}^G(\mathbf{r}_1)] \right. \right. \\ & \left. \left. \times \frac{\delta^2 F}{\delta\mathbf{Q}(\mathbf{r}_1) \delta\mathbf{Q}(\mathbf{r}_2)} \Big|_{\mathbf{Q}^G} [\mathbf{Q}(\mathbf{r}_2) - \mathbf{Q}^G(\mathbf{r}_2)] \right\rangle \right] + \dots \end{aligned} \quad (4)$$

where  $\langle \dots \rangle \equiv \int \int d\mathbf{r}_1 d\mathbf{r}_2$ . All functional derivatives on the right-hand side of (4) are evaluated at the solution  $\mathbf{Q}(\mathbf{r}) = \mathbf{Q}^G(\mathbf{r})$ . The linear term in the expansion (4) is absent since  $F_{\text{deGL}}[\mathbf{Q}^G, \delta\mathbf{Q}^G]$  is minimal at  $\mathbf{Q}^G(\mathbf{r})$ . The leading, zeroth-order term of this expansion is just the MFA free energy. It is obtained directly by the substitution  $\mathbf{Q}(\mathbf{r}) = \mathbf{Q}^G(\mathbf{r})$  into equation (3). The next-to-leading terms of (4) are called one-loop, two-loop, etc. approximations. The  $\mathbf{Q}^G(\mathbf{r})$  configuration is also known as a 'saddle point' of the Feynman integral (2).

The field  $\mathbf{Q}(\mathbf{r}) = \mathbf{Q}^G(\mathbf{r})$  is found in practice by considering individually all relevant periodic and quasi-periodic structures parametrized in terms of linear combinations of plane waves of helicity  $m$

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_m \mu_m(\mathbf{k}) \mathbf{M}_m(\mathbf{k}) \exp i\mathbf{k} \cdot \mathbf{r} \quad (5)$$

where

$$\begin{aligned} \mathbf{M}_0(\mathbf{k}) &= 6^{-1/2} \{3\hat{\mathbf{k}} \otimes \hat{\mathbf{k}} - 1\} \\ \mathbf{M}_{\pm 1}(\mathbf{k}) &= \pm \frac{1}{2} \{(\hat{\mathbf{v}} \pm i\hat{\mathbf{w}}) \otimes \hat{\mathbf{k}} + \hat{\mathbf{k}} \otimes (\hat{\mathbf{v}} \pm i\hat{\mathbf{w}})\} \\ \mathbf{M}_{\pm 2}(\mathbf{k}) &= \frac{1}{2} \{(\hat{\mathbf{v}} \pm i\hat{\mathbf{w}}) \otimes (\hat{\mathbf{v}} \pm i\hat{\mathbf{w}})\} \end{aligned} \quad (6)$$

are the spin  $L=2$  tensors represented in an orthogonal, right-handed local coordinate system  $\{\hat{\mathbf{v}}, \hat{\mathbf{w}}, \hat{\mathbf{k}}\}$  with  $\hat{\mathbf{k}}$  playing the role of the  $z$ -axis. The reality condition  $\mathbf{Q}(\mathbf{r}) = [\mathbf{Q}(\mathbf{r})]^*$  additionally implies that

$$\mathbf{M}_m(-\mathbf{k}) = (-1)^m (\mathbf{M}_m(\mathbf{k}))^* \quad (7)$$

Assuming the invariance of the expansion (5) under space group symmetries one obtains the well known selection rules, that is all symmetry allowed values of wave vectors and helicities entering the summation in the formula (5). After identifying them, the MFA free energy can now be calculated explicitly. In particular, the quadratic part reads

$$\begin{aligned} F_2 = & \frac{1}{2} \sum_{\sigma} \sum_m \{a - mdq\sigma^{1/2} \\ & + [c_1 + \frac{1}{6}c_2(4 - m^2)]q^2\sigma\} |\mu_m(\mathbf{k})|^2, \end{aligned} \quad (8)$$

where  $q = k\sigma^{-1/2}$  determines the length scale of the reciprocal lattice,  $\sigma = n_1^2 + n_2^2 + n_3^2$  ( $n_i$  being the Miller indices) and, finally,  $a = a_0(T - T')$  is the temperature.

By minimizing  $F_2$  with respect to  $q$  and  $m$  and in the units of energy, length and of  $\mathbf{Q}$  introduced by Grebel *et al.* [12] one finally arrives at [7, 12]

$$\begin{aligned} F_{\text{deGL}} &= F_2 + F_3 + F_4 \\ F_2 &= \frac{1}{2} \sum_{\sigma} \sum_m \left\{ \frac{t}{2} - \kappa^2 \left\{ \frac{m}{2^{3/2}} r\sigma^{1/2} \right. \right. \\ & \left. \left. + \left[ 1 + \frac{1}{6} \frac{c_2}{c_1} (4 - m^2) \right] \frac{1}{4} r^2 \sigma \right\} \right\} |\mu_m(\mathbf{k})|^2 \\ F_3 &= -6^{1/2} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \sum_{m, m', m''} \mu_m(\mathbf{k}) \mu_{m'}(\mathbf{k}') \mu_{m''}(\mathbf{k}'') \\ & \times \text{Tr}[\mathbf{M}_m(\mathbf{k}) \mathbf{M}_{m'}(\mathbf{k}') \mathbf{M}_{m''}(\mathbf{k}'')] \delta_{\mathbf{k} + \mathbf{k}' + \mathbf{k}'', 0} \\ F_4 &= \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \mathbf{k}'', \mathbf{k}'''}} \sum_{\substack{m, m' \\ m'', m'''}} \mu_m(\mathbf{k}) \dots \mu_{m'''}(\mathbf{k}''') \\ & \times \text{Tr}[\mathbf{M}_m(\mathbf{k}) \mathbf{M}_{m'}(\mathbf{k}')] \text{Tr}[\mathbf{M}_{m''}(\mathbf{k}'') \mathbf{M}_{m'''}(\mathbf{k}''')] \\ & \times \delta_{\mathbf{k} + \mathbf{k}' - \mathbf{k}'' + \mathbf{k}''', 0}, \end{aligned} \quad (9)$$

where  $r$  is the absolute value of the wave vector  $\mathbf{k}$  that minimizes the quadratic part of the free energy (9).

Note that the functional (3) depends only on three parameters: the reduced temperature  $t$ , the reduced chirality  $\kappa$ , which is proportional to the wave vector of the cholesteric phase, and the relative elastic constant  $c_2/c_1$ . The remaining two parameters ( $\beta, \gamma$ ), present in (3), are redundant. For  $F_{\text{deGL}}$  to be positive definite we additionally require that  $c_2/c_1 > -3/2$  and  $\gamma > 0$ . Due to the choice of units and due to the prolate-oblate symmetry of  $F_{\text{deGL}}$  one may always take  $\beta = \gamma = 1$  [16].

The minimization over the fields  $\mathbf{Q}(\mathbf{r})$  is thus reduced to a minimization over the amplitudes  $\mu_m(|\mathbf{k}|)$ . The most difficult parts of the calculations are the traces over spin matrices and the sums over relevant vectors  $\mathbf{k}$ . Due to these limitations, the most advanced calculations done so far were restricted to up to four leading stars of the wave vectors and to the  $m=2$  modes. The latter correspond to the low-lying branch of the excitation spectrum of the quadratic part of the free energy (9). The last approximation makes the term proportional to  $c_2/c_1$  vanish and, consequently, the only parameters left are  $t$  and  $\kappa$ . Hence, by minimizing  $F_{\text{deGL}}$  with respect to the amplitudes  $\mu_2(\sigma)$ , a *universal* phase diagram is obtained [12], which is shown as the inset in figure 1.

As already discussed in the previous section, the theoretical phase diagram of figure 1 yields an incorrect identification of the structure of BPII and cannot account for many trends observed experimentally. Hence, chiral liquids cannot be fully understood without more advanced calculations that go beyond mean-field. It is believed, however, that the statistical field theory as represented by equation (2) is a correct description of BPs. In the next section we shall propose an extension

of the de Gennes–Ginzburg–Landau theory that may be relevant for the issues discussed. A possible explanation of the BPIII structure will also be given.

### 3. De Gennes–Ginzburg–Landau free energy in the presence of bond order

Thermal fluctuations, which are not taken into account in the mean field analysis, may change the theoretical phase diagrams in an essential way. For a demonstration, let us consider the so called high chirality limit (HCL) ( $\kappa \rightarrow \infty$ ) of the free energy, equation (2), [6, 9] (see also [1]), in which fluctuations of the tensor field  $\mathbf{Q}$  become especially important and the mean field results certainly do not hold. In this limit the bulk part of  $F_{\text{deGL}}/\kappa^2$  vanishes and the ground state is determined by the quadratic part,  $F_2$ , of the free energy. It is given as an arbitrary linear combination of the states  $m=2$  on the spherical shell  $|\mathbf{k}| = \text{const.}$  [1]. Though this continuous degeneracy of  $\mathbf{Q}$  is partly removed for finite chiralities by the bulk free energy, it is clear that in the presence of thermodynamic fluctuations no periodic or quasi-periodic structure should be stable for very high chiralities.

Hence, if we start at very large chiralities, at least two possibilities for the structure of BPIII appear likely. One possibility is that of another isotropic liquid, modelled predominantly by the modes of the shell  $|\mathbf{k}| \approx \text{const.}$  It is characterized by  $|\mathbf{k}| \approx \text{const.}$ ,  $\mathbf{Q} \equiv 0$  and  $v^{-1} \int d^3\mathbf{x} \text{Tr} \mathbf{Q}^2 \neq 0$  or, alternatively, by  $\Lambda^{\text{micro}} = v^{-1} \int d^3\mathbf{r} e_{\alpha\beta\gamma} Q_{\alpha\rho}(\mathbf{r}) \partial_\beta Q_{\gamma\rho}$  [9] (the last two averages being different from their values in the isotropic liquid). Here the overline denotes the thermal average over all fields  $\mathbf{Q}(\mathbf{r})$ . The role of the bulk part of  $F_{\text{deGL}}$  is to restrict the norm of  $\mathbf{Q}$ .

In the isotropic model, which certainly is relevant for very high chiralities, all symmetry elements of a space group are lost due to the strong thermodynamic fluctuations. But with lowering the chirality, fluctuations should become less important and consequently some symmetry elements which are common to many space groups (like those forming a factor group), may survive. For the BPIII structure such symmetry elements show up in a long range orientational order while a periodic (or a quasi-periodic) ordering is absent. The long range orientational order would appear between macroscopically correlated regions in the  $Q_{\alpha\beta}(\mathbf{r})$  space. A similar possibility for atomic crystals has been suggested by Nelson and Toner [14], Kosterlitz *et al.* [18] and Halperin *et al.* [19] and is commonly referred to as a bond oriented phase. In the bond oriented phase of atomic crystals the translational symmetry is lost but the system remembers the directions of crystallographic axes present in the solid. The phase is obtained in the process of defect mediated melting of a low temperature

crystalline structure. Interestingly, a quasi two-dimensional structure with these properties has indeed been discovered in liquid crystals and is known as a hexatic phase [19]. It arises in the process of defect mediated melting of the smectic B phase. If a similar scenario is possible in chiral liquid crystals, one would get a new type of isotropic liquid with long range *three-dimensional* bond orientational order of octahedral symmetry, which is a common factor group of the BPI and BPII structures. The bond oriented liquid would be obtained as a result of (defect mediated) melting of BPI or BPII cubic, dielectric superlattices [9, 11].

Further implications of the presence of fluctuations on the spherical shell of  $|\mathbf{k}| = \text{const.}$  have been studied for a scalar order parameter field by Brazovski *et al.* (see, e.g. [13] and references therein). They showed that the mean field transition temperature between the isotropic liquid and a structure of a space group symmetry  $G$  is depressed. It may also happen that the space group symmetry stabilized in the presence of fluctuations is different from its mean field counterpart. Such calculations for the BPI and BPII structures will be reported elsewhere. They, however, leave open the question of the structure of BPIII.

In this section we shall investigate some consequences of the presence of cubic bond orientational order on the structural stability of the Blue Phases. We start an analysis by introducing the relevant bond orientational order parameters and the effective free energy. Generalizing the results of Nelson and Toner [14] and those of Jarić [15], we introduce a bond orientational tensor order parameter field  $B_{\alpha\beta\mu\nu}(\mathbf{r}, \hat{\mathbf{n}})$  (which must be a tensor of rank, at least, four):

$$B_{\alpha\beta\mu\nu}(\mathbf{r}, \hat{\mathbf{n}}) = \overline{B_{\alpha\beta\mu\nu}^{\text{micro}}(\mathbf{r}, \hat{\mathbf{n}})} \\ = \frac{1}{v} \int d^3\mathbf{x} w(\mathbf{x}) Q_{\alpha\beta}(\mathbf{r} + \mathbf{x}) \int n^2 dn Q_{\mu\nu}(\mathbf{r} + \mathbf{x} + \mathbf{n}) w(\mathbf{n}), \quad (10)$$

where  $w(\mathbf{x})$  is a coarse-graining function.

As seen from equation (10) the bond orientational order accounts for *non-local properties* of the system. It approximates orientational correlations between  $\mathbf{Q}(\mathbf{r})$  and  $\mathbf{Q}(\mathbf{r} + \hat{\mathbf{n}})$  along the direction  $\hat{\mathbf{n}}$  by an effective order parameter  $B_{\alpha\beta\mu\nu}(\mathbf{r}, \hat{\mathbf{n}})$ . The leading term in  $\mathbf{B}(\mathbf{r}, \hat{\mathbf{n}})$ , which we call the  $\mathbf{B}$ -tensor, is obtained from the expansion into spherical harmonics and into plane waves of equation (10)

$$\overline{B_{\alpha\beta\mu\nu}^{\text{micro}}} \approx \frac{1}{v} \int d^3\mathbf{r} \int d^3\mathbf{x} \int d^3\mathbf{y} Q_{\alpha\beta}(\mathbf{r} + \mathbf{x}) Q_{\mu\nu}(\mathbf{r} + \mathbf{y}) w(\mathbf{x}) w(\mathbf{y}) \quad (11)$$

It is now very convenient to decompose  $\mathbf{B}$  into  $SO(3)$ -irreducible tensors  $\mathbf{B}^L$  of components  $B_{\alpha\beta\mu\nu}^L$ . Only three

tensors, characterized by  $L=0, 2$  and  $4$ , are obtained. For cubic symmetry, which we analyze here, the only irreducible part of  $\mathbf{B}$  is  $\mathbf{B}^4$ . At experimental level, the tensor  $\mathbf{B}^4$  is associated with the cubic part of the non-linear dielectric susceptibility tensor. It is responsible for the alignment of BPI and BPII crystals by an electric field, as has been shown experimentally by Pierański *et al.* [20].

To gain insight into a possible influence of the  $\mathbf{B}^4$ -field on the stability of the Blue Phases we formally replace the ‘microscopic’ free energy (2) by an approximate, effective free energy functional  $F[\mathbf{Q}^G, \mathbf{B}^4]$  [9]

$$\begin{aligned} \mathcal{F}[\mathbf{Q}^G(\mathbf{r}), \mathbf{B}^4] &\equiv F = -k_B T \ln \int D\mathbf{Q}(\mathbf{r}) \delta(\mathbf{B}^4 - \mathbf{B}^{4,\text{micro}}) \\ &\times \exp \left\{ \frac{-F_{\text{deGL}}[\mathbf{Q}(\mathbf{r}), \partial\mathbf{Q}(\mathbf{r})]}{k_B T} \right\} \\ &\approx F_{\text{deGL}}[\mathbf{Q}^G(\mathbf{r})] + F_{\text{coupl}}[\mathbf{Q}^G(\mathbf{r}), \mathbf{B}^4] \\ &+ F_{\text{bond}}[\mathbf{B}^4]. \end{aligned} \quad (12)$$

The procedure is justified since all phase transitions involving Blue Phases are weakly first order. The equilibrium forms of the tensors  $\mathbf{Q}^G(\mathbf{r})$  and  $\mathbf{B}^4$  are, as usual, determined by minimizing  $F$ . If this formalism is indeed applicable to the Blue Phases, the minimization of  $F$  should yield an order parameter  $\mathbf{Q}^G(\mathbf{r})$  non-zero in BPI and BPII, but zero in BPIII, while the bond orientational order parameter  $\mathbf{B}^4$  should be non-zero in all Blue Phases. We shall see that these general features are indeed recovered from the effective free energy (12). Furthermore, within the minimal coupling scheme for  $F$  the BPIII could, in principle, be uniquely identified with a cubic bond ordered structure.

Besides the  $F_{\text{deGL}}$  part of  $F$ , already accounted for in equation (2), there are two extra parts in equation (12), denoted  $F_{\text{coupl}}$  and  $F_{\text{bond}}$ . The  $F_{\text{coupl}}$  part represents the coupling between the ground state  $\mathbf{Q}^G(\mathbf{r})$  of the space group symmetry  $G$  and the bond orientational order parameter  $\mathbf{B}$ .  $F_{\text{bond}}$  accounts for structures which do not show spatial modulation.

To obtain the minimal coupling form for  $F_{\text{bond}}$ , please note that the  $L=4$  irreducible part  $\mathbf{B}^4$  of the cartesian tensor  $\mathbf{B}$  is equivalent to a nine-dimensional spherical vector order parameter  $\Omega^4$  of components  $\Omega_m^4$  ( $m = -4, \dots, 4$ )

$$B_{\alpha\beta\gamma\delta}^4 = \sum_{m=-4}^4 (-1)^m \Omega_m^4 \mathbf{M}_{-m}^4(\hat{\mathbf{u}}) \quad (13)$$

where  $\mathbf{M}^4(\hat{\mathbf{u}})$  are the irreducible basis tensors of spin  $L=4$ . They are defined with respect to an orthonormal, right-handed tripod  $\{\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3 \equiv \hat{\mathbf{u}}\}$ —the Goldstone mode of  $F_{\text{bond}}$ .

The lowest order, analytically independent and  $SO(3)$

symmetric invariants, which enter the expansion of  $F_{\text{bond}}$ , read [15]

$$I_4^2(\Omega^4) = \sum_{m=-4}^4 (-1)^m \Omega_m^4 \Omega_{-m}^4 \quad (14)$$

$$I_4^3(\Omega^4) = \sum_{m_1 m_2 m_3} \begin{pmatrix} 4 & 4 & 4 \\ m_1 & m_2 & m_3 \end{pmatrix} \Omega_{m_1}^4 \Omega_{m_2}^4 \Omega_{m_3}^4 \quad (15)$$

$$I_4^{4,0}(\Omega^4) = I_4^2(\Omega^4)^2 \quad (16)$$

$$I_4^{4,1}(\Omega^4) = \frac{\partial I_4^3}{\partial \Omega^4} \cdot \frac{\partial I_4^3}{\partial \Omega^4}, \quad (17)$$

where

$$\begin{pmatrix} 4 & 4 & 4 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

are the  $3j$ -symbols. Using equations (14) to (17) the expression for  $F_{\text{bond}}$  takes the following form:

$$\begin{aligned} F_{\text{bond}} &= \frac{1}{2} \bar{a}_2 I_4^2(\Omega^4) + \frac{1}{3} \bar{a}_3 I_4^3(\Omega^4) + \frac{1}{4} \sum_{i=0}^{4/2-1} \bar{a}_{e,i} I_4^{4,i}(\Omega^4) \\ &\equiv \frac{1}{2} \bar{a}_2 B_{\alpha\beta\gamma\delta}^4 B_{\alpha\beta\gamma\delta}^4 + \frac{1}{3} \bar{a}_3 B_{\alpha\beta\gamma\delta}^4 B_{\alpha\beta\mu\nu}^4 B_{\gamma\delta\mu\nu}^4 \\ &+ \frac{1}{4} \bar{a}_{4,0} (B_{\alpha\beta\gamma\delta}^4 B_{\alpha\beta\gamma\delta}^4)^2 + \frac{1}{4} \bar{a}_{4,1} B_{\alpha\beta\gamma\delta}^4 B_{\gamma\delta\mu\nu}^4 B_{\mu\nu\rho\sigma}^4 B_{\rho\sigma\alpha\beta}^4. \end{aligned} \quad (18)$$

The minima of  $F_{\text{bond}}$  are located in invariant subspaces of the nine-dimensional space  $\{\Omega^4\}$  associated with the subgroup  $G$  of  $SO(3)$ :

$$g\Omega^4 = 1 \cdot \Omega^4 \quad \forall g \in G < SO(3) \quad (19)$$

Clearly, the  $SO(3)$  irreducible representation  $L=4$  becomes reducible with respect to  $G < SO(3)$  and the corresponding basis functions of the invariant subspaces are obtained using the projection operator

$$P_{kk}^x Y_4^4 \equiv \frac{d_x}{|G|} \sum_{g \in G} D_{kk}^{(x)}(g) \cdot D(g) Y_4^4 \quad (20)$$

where  $d_x = 1$  is the dimension of the unity representation  $D_{kk}^{(x)}(g) \equiv 1$  of the subgroup  $G$ , where  $|G|$  is the group order and  $D(g)$  the three-dimensional representation of  $g$  in the real space. The number of independent basis functions yields the dimension of the invariant sub-space. Jarić showed [15] that for a minimal coupling theory only structures with symmetries corresponding to sub-spaces of the lowest dimension can be accessed via a phase transition from the isotropic phase. This implies that for the order parameter  $\mathbf{B}^4$  and for the free energy (18) only three low symmetry structures are accessible from the isotropic liquid: (i) an octahedral  $O_h$  (one-dimensional invariant sub-space), (ii) a uniaxial  $D_{\infty h}$  (one-dimensional invariant sub-space) and (iii) a  $D_{4h}$  (two-dimensional invariant sub-space).

The lowest order non-trivial terms of the  $F_{\text{coupl}}$  part

are found in a similar way. There is only one term of the lowest order [9] which reads

$$F_{\text{coupl}}(\mathbf{Q}(\mathbf{r}), \mathbf{B}^4) = -\frac{\lambda}{3} B_{\alpha\beta\gamma\delta}^4 \int d^3\mathbf{r} [Q_{\alpha\beta}(\mathbf{r})Q_{\gamma\delta}(\mathbf{r}) + Q_{\alpha\gamma}(\mathbf{r})Q_{\beta\delta}(\mathbf{r}) + Q_{\alpha\delta}(\mathbf{r})Q_{\gamma\beta}(\mathbf{r})]. \quad (21)$$

The effective parameters entering equations (18) and (21) depend on 'bare' parameters of the expansion (9). This dependence could, at least theoretically, be found from the formula (12). An alternative way, which we follow in this paper, is to assume some simple temperature and chirality dependence for these coefficients. The only condition that must be fulfilled is that the free energy (18) should be stable with respect to an unlimited growth of  $\mathbf{B}^4$ . In the next section we shall be concerned with an in-depth analysis of the phase diagrams that follow from the free energy expansion (12).

#### 4. Results

We start our discussion by concentrating on general results that are independent of the detailed form of the tensor  $\mathbf{Q}^G(\mathbf{r})$ . First of all the form of the coupling (21) has the consequence that the cubic bond orientational order parameter  $\mathbf{B}^4$  is always induced by the periodic ground state  $\mathbf{Q}^G(\mathbf{r})$ , whereas the structure  $\mathbf{Q}^G(\mathbf{r})$  is not automatically generated by the bond order. The bond order can condense before any spatial periodicity of  $\mathbf{Q}^G(\mathbf{r})$  is established in the system. The corresponding structure could be associated with BPIII. If we just restrict ourselves to this possibility, by an appropriate choice of the coupling constants in (18) and (21), then the minimization of the bond part is carried out independently of  $F_{\text{deGL}}$  and  $F_{\text{coupl}}$ . The results of such a minimization are summarized below. As already argued in the previous section the minimal coupling theory (18) generates only three bond-ordered structures: (I) the octahedral (cubic)  $O_h$ , (II) the uniaxial  $D_{\infty h}$  and (III) the  $D_{4h}$  that are accessible from the isotropic liquid via a phase transition [15]. The bond-orientational phase diagram is dominated by the octahedral structure, which can be accessed from the isotropic phase through either a *first-order phase transition* or a *tricritical continuous transition*. The uniaxial phase is accessed only through a first-order phase transition. The structure of  $D_{4h}$  symmetry can only be accessed through a second-order phase transition and requires  $\bar{a}_2 = \bar{a}_3 = 0$ , which makes it much less probable than  $D_{\infty h}$  and  $O_h$ . Since  $D_{\infty h}$  and  $O_h$  symmetries are mutually exclusive in parameter space and since  $D_{\infty h}$  symmetry has not been detected experimentally in BPs, we conclude that within the concept of bond orientational order, the most probable candidate

for the structure of BPIII is indeed the one of  $O_h$  symmetry. From now on we shall exclusively be concerned with this case. As the symmetries on both sides of the phase transition are different, the model cannot account for a suggested super-critical conversion of BPIII to the isotropic phase [5].

Precise equilibrium forms of the tensors  $\mathbf{Q}^G(\mathbf{r})$  and  $\mathbf{B}^4$  may, as usual, be determined by minimizing  $F$ . In order to make calculations of the same accuracy as the ones carried out by Grebel, Hornreich and Shtrikman [12], we take up to four leading stars of wave vectors  $\mathbf{k}$  for cubic space group symmetries. For each star we select only  $m=2$  modes, which correspond to the low-lying branch of the excitation spectrum of the quadratic part of  $F_{\text{deGL}}$  [12]. Clearly, the cross-coupling term (21) together with the terms of  $F_{\text{deGL}}$  are directly responsible for the stabilization of different cubic structures.

Assuming octahedral symmetry for the cubic bond orientational order parameter,  $\mathbf{B}^4$ , equation (20) gives

$$B_{\alpha\beta\gamma\delta}^4 = B_0 2^{1/2} 5^{1/2} 7^{1/2} \times \{(\frac{5}{14})^{1/2} [\mathbf{M}_4^4(\hat{\mathbf{u}}) + \mathbf{M}_{-4}^4(\hat{\mathbf{u}})] + \mathbf{M}_0^4(\hat{\mathbf{u}})\}_{\alpha\beta\gamma\delta} = B_0 \tilde{B}_{\alpha\beta\gamma\delta}^4. \quad (22)$$

After substituting (22) to  $F_{\text{coupl}}$  and  $F_{\text{bond}}$  both parts of the free energy  $F$  simplify considerably to yield

$$F_{\text{bond}} = \frac{1}{4} a_2 (t, \kappa^2) B_0^2 - a_3 B_0^3 + a_4 B_0^4, \quad (23)$$

and

$$F_{\text{coupl}} = -\frac{\lambda}{3} B_0 \sum_{\mathbf{k} \in G} (\mu_2(k))^2 \tilde{B}_{\alpha\beta\gamma\delta}^4(\{\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}\}) \tilde{E}_{[\alpha\beta\gamma\delta]}(\mathbf{k}). \quad (24)$$

In the last formula

$$\tilde{E}_{[\alpha\beta\gamma\delta]}(\mathbf{k}) = (\mathbf{M}_2(\mathbf{k}))_{[\alpha\beta} (\mathbf{M}_{-2}(\mathbf{k}))_{\gamma\delta]} \quad (25)$$

is the numerical tensor and  $[\alpha\beta\gamma\delta]$  denotes symmetrization over indices  $\alpha\beta\gamma\delta$ . For cubic space groups, each of the numerical tensors (25) has an octahedral symmetry with four-fold symmetry axes parallel to the laboratory frame system. The question to be answered first is how the local tripod (Goldstone mode)  $\{\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}\}$  is oriented with respect to these four-fold axes. We consider two possibilities. The first one is to minimize the coupling term with respect to the tensor orientation. This is certainly a thermodynamically correct procedure and can be done exactly with the help of  $SU(2)$  Cayleigh–Klein parametrization of the tripod. For the cubic space groups, the minimum of  $F_{\text{coupl}}$  is attained for the tripod taken parallel either to the  $[100]$  directions or to the  $[122]$  directions. More specifically, if the numerical tensors are exclusively built out of the  $[n00]$  vectors for  $\lambda B_0 > 0$ , the minimum generally corresponds to the tripod oriented along  $[100]$  and for  $\lambda B_0 < 0$  to the



tripod oriented along  $[122]$ . The numerical tensors built out of the  $[nn0]$  or the  $[nn(2n)]$  stars behave in the opposite way. If we analyse both cases we arrive at simple expressions for the coupling term, (21), which for  $BPI(O^8)$ ,  $BPII(O^2)$  and for  $O^5$  structures read, respectively

$$\text{Min} \{ \lambda B_0 [\mu_2^2(4) - \frac{1}{4} [\mu_2^2(2) + \mu_2^2(6) + \mu_2^2(8)]], \quad (26)$$

$$- \frac{13}{27} \lambda B_0 [\mu_2^2(4) - \frac{1}{4} [\mu_2^2(2) + \mu_2^2(6) + \mu_2^2(8)]] \}$$

$$\text{Min} \{ \lambda B_0 [\mu_2^2(1) - \frac{1}{4} \mu_2^2(2)], \quad (27)$$

$$- \frac{13}{27} \lambda B_0 [\mu_2^2(1) - \frac{1}{4} \mu_2^2(2)] \}$$

$$\text{Min} \{ -\lambda B_0 \frac{1}{4} [\mu_2^2(2) + \mu_2^2(6) + \mu_2^2(8)], \quad (28)$$

$$\frac{13}{27} \lambda B_0 \frac{1}{4} [\mu_2^2(2) + \mu_2^2(6) + \mu_2^2(8)] \},$$

where the first (second) term under  $\text{Min}(\dots)$  corresponds to the Goldstone mode parallel to  $[100]$  ( $[122]$ ) directions.

For the cholesteric phase and for  $\lambda B_0 > 0$  the vector  $\hat{\mathbf{u}}$  of the tripod is oriented along the  $[100]$  direction. For  $\lambda B_0 < 0$  it is degenerate on a cone forming an angle of 45 degrees with the  $[100]$  direction. For these cases the expression for the coupling reads

$$\text{Min} \{ -\lambda B_0 [6\mu_0^2(0) + 2\mu_2^2(2)], \frac{1}{4} \lambda B_0 [6\mu_0^2(0) + 2\mu_2^2(2)] \} \quad (29)$$

As seen from equations (26) to (29) the minimization of the total free energy for  $\lambda B_0 < 0$  may stabilize symmetries which are not observed experimentally in chiral liquid crystals. It is not clear whether this is an artefact of the truncation imposed on the expansion (12) or whether it is inherent to the model. Hence, as a second possibility, we shall discuss the case when the tripod is just fixed parallel to the cubic  $[100]$  directions, without performing the minimization described above. It certainly yields results that are consistent with the orientation of the tensor  $\mathbf{B}^4$  found in experiments of Pierański *et al.* [20]. In both cases we introduce a linear dependence of the parameter  $a_2(t, \kappa^2)$  on  $t$  and  $\kappa^2$ :

$$a_2(t, \kappa^2) = \tilde{a} \cdot (t - \tilde{h} \kappa^2) - \tilde{\tau} \quad (30)$$

Furthermore, as the scale of  $B_0$  in equation (23) is arbitrary, we introduce units in which  $a_4 = 1$ . The remaining parameters of the model will either be assumed constant or chirality dependent.

For arbitrary  $(\kappa, t)$  and for fixed values of the material parameters, the numerical part of the minimization of the free energy over the real amplitudes  $\mu_m(|\mathbf{k}|)$  of the expansion (12) is now done by a combination of the steepest descent and the simplex methods.

Two typical phase diagrams for the case when the angle between  $\mathbf{Q}(\mathbf{r})$  and  $\mathbf{B}^4$  is minimized according to equations (26) to (29) are shown in figures 2 and 3. The

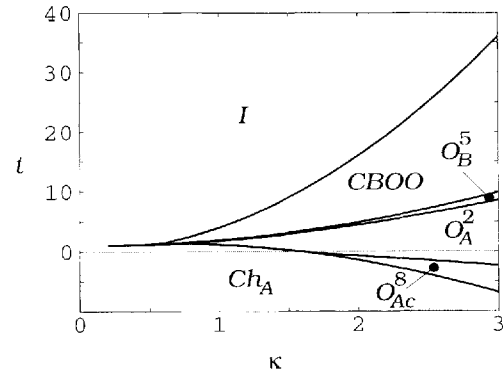


Figure 2. Phase diagram for the case where orientation of  $\mathbf{B}^4$  is found from the formulae (26) to (29). The parameters assumed are:  $\lambda = 0.002$ ,  $\tilde{a} = 1.0$ ,  $\tilde{b} = 4.0$ ,  $\tilde{\tau} = -1.0$ ,  $b = c = 1.0$ . The phase diagram is very similar to the phase diagram of figure 1 of Grebel *et al.* The phases indexed by 'B' have bond orientational order in the  $[112]$  direction.

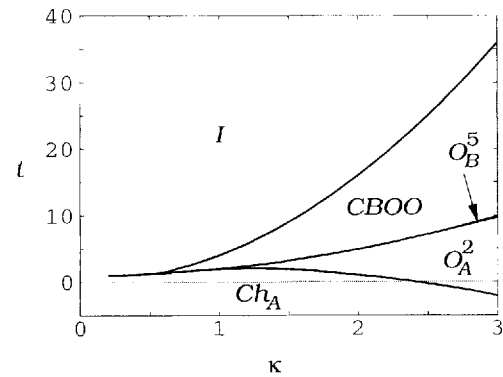


Figure 3. Phase diagram for the case where orientation of  $\mathbf{B}^4$  is found from the formulae (26) to (29). The parameters assumed are:  $\lambda = 0.02$ ,  $\tilde{a} = 2.0$ ,  $\tilde{b} = 4.0$ ,  $\tilde{\tau} = -1.0$ ,  $b = c = 1.0$ . Note that stabilities of  $O^8$  and of  $O^5$  are correlated.

diagram of figure 2, obtained for small  $\lambda$ , is very similar to the diagram of Grebel *et al.* [12]. In particular the  $O^5$  structure is still present. For higher coupling strengths (figure 3) the  $O^8$  and the  $O^5$  structures disappear.

To answer the question—what structure of a space group symmetry can transform into the bond ordered phase via a phase transition?—we take the purely bond ordered phase as a reference and fix the value of  $\lambda B_0$  in the other phases. Now we check which phase shows a transition to the bond ordered phase for that value of  $\lambda B_0$ . Typical results as function of chirality are given in figure 4. Note that there is no region where  $O^8$  shows a direct transition to the bond ordered phase. The diagram is dominated by a uniaxial nematic phase, obtained from the cholesteric phase when  $\mu_2(\sigma = 2) \equiv 0$ .

From figure 4 we can conclude that within the approximations (18) and (21) it is not possible to realize

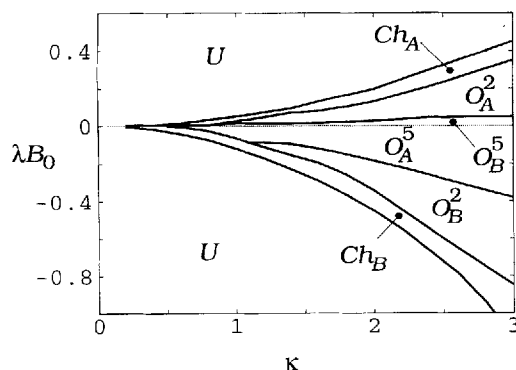


Figure 4. Phases with a direct transition to the bond ordered phase. *U* denotes a uniaxial nematic phase obtained from the cholesteric free energy as described in the text.

a direct phase transition between BPI and the bond ordered phase and that the  $O^5$  structure can only be shifted off the diagram for high coupling strengths  $\lambda$  (see also phase diagrams of figures 2 and 3). Similar results hold true for the phase transition to the isotropic phase. Again the  $O^5$  structure is stable for small  $\lambda$ s and the BPI does not show a direct transition to the isotropic state.

This behaviour seems universal for the cubic bond model. It is further illustrated in figure 5, where we present a typical phase diagram in the  $(\lambda, t)$  plane. Again BPI ( $O^8$ ) is the first phase to vanish. For higher coupling strengths  $\lambda$ , the  $O^5$  structure is also removed. Note that the latter case corresponds to that which we found within the two-stars approximation [9].

Now we shall discuss the second case when the Goldstone mode is made parallel to the  $[100]$  directions, see figure 6. It is then possible to consider negative values of the coupling strength  $\lambda B_0$ . In this case the minimization over the Goldstone mode would give phases with a ‘wrong’ orientation of the bond order tensor. Interestingly, as shown in figure 7, the stability

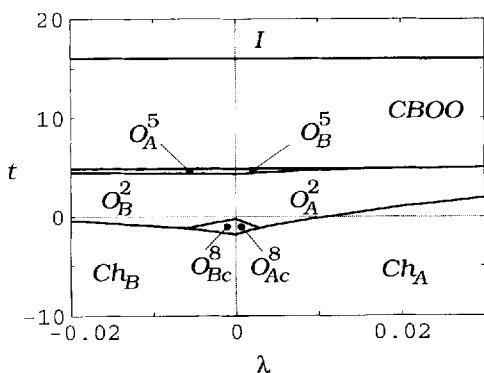


Figure 5. Dependence of the relative strength of the different phases on the coupling strength for the case where the orientation of  $\mathbf{B}^4$  is not fixed to  $[100]$ . Parameters:  $\bar{a} = 2.0$ ,  $\bar{b} = 4.0$ ,  $\bar{\tau} = -1.0$ ,  $b = c = 1.0$ ;  $\kappa = 2.0$  fixed.

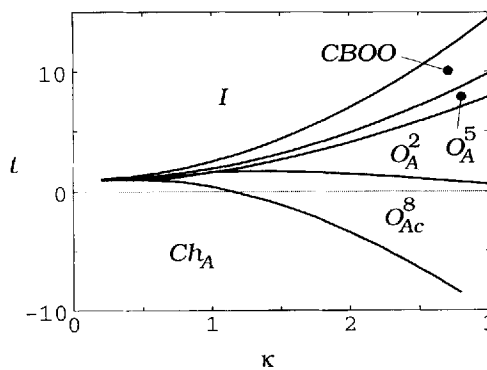


Figure 6. Phase diagram for the bond order tensor oriented parallel to the  $[100]$  direction. The parameter  $\lambda$  is taken negative:  $\lambda = -0.01$ . The remaining parameters are:  $\bar{a} = 1.0$ ,  $\bar{b} = 1.5$ ,  $\bar{\tau} = 0.0$ ,  $b = c = 1.0$ . For small chiralities between  $O_{Ac}^8$  and  $O_A^5$  there is a very small region of  $O_{Ab}^8$ , not labelled in the diagram for the sake of clarity.

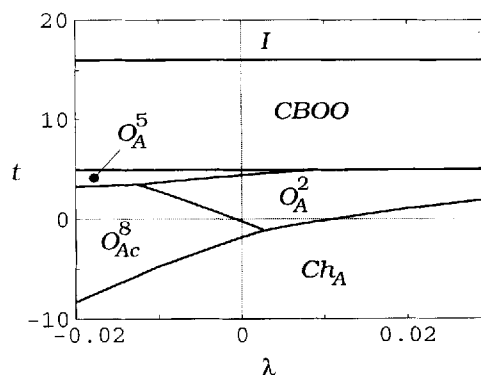


Figure 7. Dependence of the relative strength of the phases on the coupling strength when the orientation of the bond order is fixed. Parameters are:  $\bar{a} = 2.0$ ,  $\bar{b} = 4.0$ ,  $\bar{\tau} = -1.0$ ,  $b = c = 1.0$ ;  $\kappa = 2.0$  fixed.

of BPI against that of BPII is now considerably enhanced and overall trends agree with what we observe experimentally. For even higher coupling strengths, the  $O^2$  structure is shifted to higher chiralities and finally it vanishes. The same trends are also observed for the  $O^5$  structure.

From the analysis as given (see especially figures 4, 5, 7), it becomes clear that details of the phase diagrams should depend on the temperature and chirality variation of the parameters in  $F_{\text{coupl}}$  and  $F_{\text{bond}}$ . While the temperature dependence is hard to calculate and we are forced to use a simple Landau assumption equation (30), the chirality dependence seems to follow general rules.

To see this let us turn again to high chirality limit. As already argued before, the quadratic part of the free energy is proportional to  $\kappa^2$  (9), while the cubic and the fourth order free energies are of order  $\kappa^0$ . The  $\mathbf{B}^4$

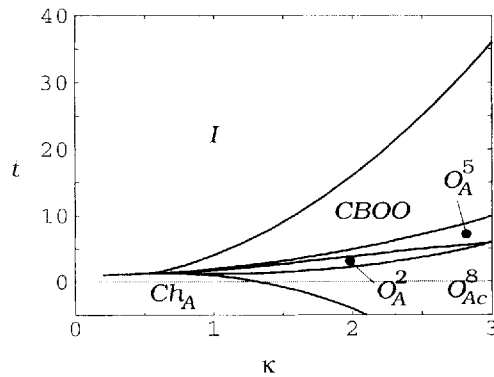


Figure 8. The  $\kappa^2$  model. The parameters are:  $\tilde{a}=2.0$ ,  $\lambda = -0.002$ ,  $\tilde{b}=4.0$ ,  $\tilde{\tau} = -1.0$ ,  $b=c=1.0$ . One can see, that  $O^2$  vanishes for high chiralities in agreement with experiment.

dependent part is then of order  $\kappa^{2n}$  where  $n$  takes one of the values 1, 0,  $-1$ ,  $-2, \dots$ . As negative values of  $n$  are inconsistent with the assumption that bond order is induced by fluctuations, we are left with  $n=1$  and  $n=0$ . The second case has already been studied, while the first one tells us that all  $\mathbf{B}^4$ -dependent terms should be multiplied by the factor  $\kappa^2$ . The corresponding phase diagram is shown in figure 8.

Now BPII is no longer present for high chiralities, in agreement with experimental results. On the other hand the  $O^5$  is enhanced as compared to the standard cases.

Finally we shall discuss the bond order structure of the cholesteric phase. The minimization of the bond part of the free energy shows that for  $\lambda B_0 > 0$ , the  $D_\infty$  symmetry is indistinguishable from the  $O_h$  cubic order. For  $\lambda B_0 < 0$ , the cubic bond order wins in the cholesteric phase. On the other hand, in the cubic Blue Phases the bond order tripod is oriented parallel to  $[122]$  directions, thus reducing the cubic symmetry to tetragonal. Neither of these symmetries has been observed experimentally in Blue Phases in the absence of an external field.

## 5. Conclusions

We have calculated phase diagrams of the Blue Phases using the recently proposed theory of cubic bond order [9]. We generalized the previous work by including more stars of wave vectors  $\mathbf{k}$  in the expansion of  $\mathbf{Q}^G(\mathbf{r})$  (two-stars calculations in [9] versus four stars calculations here), in order to be consistent with the work by Grebel *et al.* [12]. A second motivation of this work has been to provide a detailed analysis of the phase diagrams.

An important point made in [12] was that the free energy of Blue Phases is extremely sensitive to details of parametrization of the  $\mathbf{Q}^G(\mathbf{r})$  field and that four star

calculations may differ qualitatively from the two star ones. Our calculations also support this observation.

Within the proposed theory the cubic bond order is stabilized before any space group symmetry becomes relevant. This implies that the cubic bond oriented phase is a natural candidate for the structure of BPIII and indeed it could be stabilized in this part of the phase diagram where normally BPIII appears. The calculations also preserve the symmetries of BPI and BPII and improve the phase diagram, although the limited stability of BPII cannot be reproduced. The model may destabilize the artificial  $O^5$  structure, which appears at lower temperatures, but unfortunately BPI is also destabilized in this case. By fixing the orientation of the  $\mathbf{B}^4$ -tensors in the  $[100]$  direction and turning to negative  $\lambda$ s it is possible to enhance the stability of BPI over BPII, in agreement with the experiment. However the problem of the stable  $O^5$  structure is still left open.

Though currently available experimental data are indicating that the isotropic model [4, 5] may be more relevant for the structure of BPIII, the situation is not fully clear. First of all the field  $\mathbf{B}^4$  certainly is important for a correct description of the Blue Phases. This has already been proven by Pierański *et al.* [20] who showed that such an order parameter is necessary to account for the orientation of crystals of Blue Phases by a weak electric field. The position of a broad selective reflection band in BPIII, which is close to the  $[100]$  peak of BPII, also seems to be in favour of this suggestion. Furthermore, we showed recently [21] that the coupling between the bond orientational order parameter and the alignment tensor field of the cubic ground states allows one to account for the anomalous electrostriction observed in cubic Blue Phases.

It seems then, that the cubic bond order is highly relevant for the description of the Blue Phases. The question to be answered experimentally is whether it can form long range ordering in BPIII or whether it only exists locally. Unfortunately at theoretical level a direct comparison of the free energies of the isotropic model [10, 11] and of the cubic bond model is not possible at present.

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