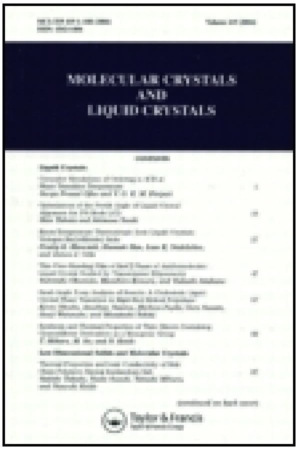

# Molecular Crystals and Liquid Crystals

# Continuum Landau Model for Biaxial Nematic Liquid Crystals

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# Continuum Landau Model for Biaxial Nematic Liquid Crystals

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*We present a phenomenological theory for the homogeneous phases of nematic liquid crystals constituted by biaxial $D_{2h}$-symmetric molecules. We propose a general polynomial free-energy in two macroscopic order tensors that reproduces the mean-field phase diagram confirmed by Monte Carlo simulations [De Matteis et al., Phys. Rev. E* **72***, 041706, (2005)] and recently recognized to be universal [Bisi et al., Phys. Rev. E* **73***, 051709, (2006)] for dispersion forces molecular pair potentials enjoying the $D_{2h}$ symmetry. The requirement that the phenomenological theory comply uniquely with this phase diagram reduces considerably the admissible phenomenological coefficients, both in their number and in the ranges where they can vary.*

*We also consider a generalization of the polynomial theory in order to describe non-homogeneous phases in confined geometries of liquid crystals.*

**Keywords:** biaxial liquid crystals; Landau theory; nematic phases; phase transitions

**PACS Numbers:** 61.30.Cz; 61.30.Dk

## 1. INTRODUCTION

It was Marvin Freiser of IBM who first predicted in 1970 that long and flat molecules could form a biaxial nematic phase. Since then chemists have been attempting to synthesize such a liquid crystal. But whilst lyotropic biaxial phase was found, thermotropic biaxial

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phase proved very difficult to create. In 2004, several experimentalist groups working on this subject, published their studies of bent-core and tetrapode molecules [1–4] which suggest that their molecules may form the elusive biaxial nematic phase. In [4] it has been reported evidence of *tricritical* behaviour on the uniaxial-to-biaxial phase transition: i.e., the transition can be first- and second-order. Last year new evidence of biaxiality has been found for boomerang-shaped $C_7$ molecules [5] and also for metallomesogens [6]. In particular, in [6] the idea was to design metallomesogens likely to introduce lateral correlations to promote order in directions orthogonal to the main director and hence stabilize a biaxial nematic phase. The authors also found evidence of a direct transition to the biaxial nematic phase from the isotropic one and, moreover, first-order. These experimental findings have revived the theoretical interest for macroscopic biaxiality induced by the cooperative behavior of biaxial molecules [7], which is generally suppressed by statistical averaging in standard nematic liquid crystals. A mean-field model was put forward in [8] and further analyzed in [9–14], which builds upon Straley's general pair potential [15] for dispersion forces interactions between molecules enjoying the $D_{2h}$ symmetry. Within this model, the most general macroscopic state of a nematic liquid crystal is described by two order tensors, $\mathbf{Q}$ and $\mathbf{B}$. While $\mathbf{Q}$ is the traditional order tensor introduced by de Gennes [16], which can only describe the phase biaxiality possibly arising in the statistical orientational distribution of uniaxial molecules, $\mathbf{B}$ is the order tensor that measures at a macroscopic scale the ordering of biaxial molecules. The special symmetric interaction potential in Straley's general family studied in [8] revealed a phase diagram richer in details than the one predicted by Freiser's potential [17,18], the most notable case of Straley's general pair potential, also studied within the mean-field approximation [19]. The new features of the phase diagram included a direct isotropic-to-biaxial transition that may be either first- or second-order, depending on a model parameter in the interaction pair potential. Moreover, the secondary uniaxial-to-biaxial transition that Freiser's model predicted to be second-order can be both first- and second-order for the extended model [8]. This revealed a tricritical point along the uniaxial-to-biaxial transition line, thus, in qualitative accordance with the above mentioned experimental findings [4,20]. It was then proved in [10] that the mean-field phase diagram predicted for the symmetric potential in [8] is indeed universal within the quadrupolar approximation, as its qualitative features are common to all pair potentials in Straley's general family.

In this paper, we present a phenomenological Landau theory for homogeneous phases of biaxial nematic liquid crystals. To this end, we construct the most general invariant polynomial $\mathcal{G}$ of degree four in $\mathbf{Q}$ and $\mathbf{B}$ able to reproduce the phase diagram compatible with all Straley's general pair potentials. Within this family, the symmetric potential plays a special role in our constructing strategy. Formulating this symmetry for the general Landau potential $\mathcal{G}$ reduces the number of admissible phenomenological coefficients. However, the potential $\mathcal{F}$ thus reduced is still too general. We need to restrain the critical points of the symmetric potential $\mathcal{F}$ further and correspondingly ensure appropriate stability of the restraining criteria to obtain the desired restriction of the phenomenological coefficients.

The paper is organized as follows. In Sec. 2, we recall the basic definitions of our theory for biaxial nematics. In Sec. 3, we first posit the general potential $\mathcal{G}$ and study some of its equilibrium properties; then, one subsection is devoted to the symmetric potential $\mathcal{F}$ and to the criteria that restrain its critical points; there, we also define the stability requirements employed to confine the phenomenological coefficients of $\mathcal{F}$ and we arrive at general sufficient conditions on its coefficients for it to reproduce only the universal phase diagram of biaxial nematic liquid crystals with the general $D_{2h}$ symmetry. Another subsection is devoted to a comparison between our Landau free-energy, reduced by symmetry, and other theories present in the old and current literature. In Sec. 4, the essential ingredients are presented for positing a complete macroscopic theory which also accounts for elasticity. Finally, in Sec. 5, we summarize our main conclusions and the perspectives that our work opens.

## 2. TENSORIAL ORDER AND SCALAR INVARIANT FUNCTIONS

Our approach is theoretical but it follows the same physical ideas as in the above mentioned experiments: we consider molecules having a shape which deviates from the cylindrical one ($D_{\infty h}$-symmetry). More precisely, we assume, as molecular symmetry group, the $D_{2h}$ group. This means that in our molecule there are three mutually orthogonal mirror planes inducing inversion symmetry with respect to their intersection. It turns out that such a molecule can be described as a biaxial tensor decomposed into two traceless irreducible orthogonal components

$$\mathbf{q} := \boldsymbol{m} \otimes \boldsymbol{m} - \frac{1}{3}\mathbf{I} \quad \text{and} \tag{1a}$$

$$\mathbf{b} := \boldsymbol{e} \otimes \boldsymbol{e} - \boldsymbol{e}_{\perp} \otimes \boldsymbol{e}_{\perp}, \tag{1b}$$

where $\mathbf{I}$ is the identity tensor and $\{\boldsymbol{e}, \boldsymbol{e}_\perp, \boldsymbol{m}\}$ are three mutually orthogonal unit vectors associated with the molecular mirror planes. The tensor $\mathbf{q}$ represents the molecular axis $\boldsymbol{m}$, say the *long axis*, while $\mathbf{b}$ represents the lateral *short axes* $\boldsymbol{e}$ and $\boldsymbol{e}_\perp$. The anisotropic part of every molecular tensor has components proportional to $\mathbf{q}$ and $\mathbf{b}$. Since we are given two such microscopic tensors as molecular descriptors, then, on a macroscopic scale, the general state of the liquid crystal is described by two symmetric traceless second-rank order tensors, $\mathbf{Q}$ and $\mathbf{B}$, defined as ensemble averages of the molecular tensors $\mathbf{q}$ and $\mathbf{b}$,

$$\mathbf{Q} := \langle \mathbf{q} \rangle = \left\langle \boldsymbol{m} \otimes \boldsymbol{m} - \frac{1}{3}\mathbf{I} \right\rangle \quad \text{and} \quad \mathbf{B} := \langle \mathbf{b} \rangle = \langle \boldsymbol{e} \otimes \boldsymbol{e} - \boldsymbol{e}_\perp \otimes \boldsymbol{e}_\perp \rangle. \tag{2}$$

More precisely, since the molecules execute thermal motion, the direction of the vectors $\boldsymbol{m}$, $\boldsymbol{e}$ and $\boldsymbol{e}_\perp$ fluctuates and the brackets $\langle \cdots \rangle$ mean a statistical average. The tensor $\mathbf{Q}$ describes the orientational ordering of long molecular axes and the corresponding irreducible representation is

$$\mathbf{Q} = S\left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I}\right) + T(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y), \tag{3}$$

where $S$ is a parameter to measure how strongly the uniaxiality of the molecule manifests itself as the uniaxiality of the macroscopic phase; $T$ is an index of the strength with which the molecular uniaxiality generates the macroscopic biaxiality. At the same time the tensor $\mathbf{B}$ determines the orientational ordering of the short molecular axes

$$\mathbf{B} = S'\left(\boldsymbol{e}'_z \otimes \boldsymbol{e}'_z - \frac{1}{3}\mathbf{I}\right) + T'(\boldsymbol{e}'_x \otimes \boldsymbol{e}'_x - \boldsymbol{e}'_y \otimes \boldsymbol{e}'_y), \tag{4}$$

and, accordingly, the scalar parameter $S'$ measures how strongly the biaxiality of the molecule manifests itself as the uniaxiality of the macroscopic phase, while $T'$ represents how strongly the molecular biaxiality generates the macroscopic biaxiality. The two tensors do not necessarily share the same eigenframe but the two orthogonal bases $\{e_x, e_y, e_z\}$ and $\{e'_x, e'_y, e'_z\}$ are connected by an orthogonal transformation. Thus, up to a rigid rotation, there are *seven* independent quantities that determine the two tensors: *four* independent scalars necessary to express the corresponding eigenvalues and *three* parameters, Euler angles for instance, to describe the relative orientation of the two eigenframes. When the two eigenframes coincide we say that the two order tensors are *co-axial* or, equivalently, that they commute, i.e.

$$[\mathbf{Q}, \mathbf{B}] := \mathbf{QB} - \mathbf{BQ} = \mathbf{0}. \tag{5}$$

For this reason we set

$$\mathbf{B}_0 = S'\left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I}\right) + T'(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y), \tag{6}$$

and, in the general case, **B** is given by

$$\mathbf{B} = \mathbf{R}\mathbf{B}_0\mathbf{R}^T, \quad \mathbf{R} \in \mathsf{SO}(3). \tag{7}$$

In the common eigenframe configuration $(\mathbf{Q}, \mathbf{B}_0)$ the $D_{2h}$ molecular symmetry is conveyed to the macroscopic scale: a $D_{2h}$ phase symmetry is realized. Actually, since the off-diagonal components of both $\mathbf{Q}$ and $\mathbf{B}_0$ vanish, then the two order tensors are invariant under the action of $D_{2h}$ group like the microscopic tensors $\mathbf{q}$ and $\mathbf{b}$. The occurrence of the common eigenframe configuration is quite reasonable when no distorcing external causes are present in the liquid crystal like, for instance, *curvature elasticity* or/and external fields.

In the Landau theory of phase transitions one considers an effective free-energy $\mathcal{G}$ whose symmetry group $\mathsf{G}$ and degree $d$ depend on the system under consideration; generally speaking, $\mathcal{G}$ is the most general $\mathsf{G}$-invariant polynomial of degree $d$ depending on the order parameters involved. Thus, we aim at constructing the most general invariant polynomial function $\mathcal{G}$ of the two order tensors. The symmetry group is the special orthogonal group $\mathsf{SO}(3)$. This function represents the most general frame-indifferent bulk free-energy associated with biaxial nematic liquid crystals

$$\mathcal{G}(\mathbf{Q}, \mathbf{B}) = \mathcal{G}(\mathbf{R}\mathbf{Q}\mathbf{R}^T, \mathbf{R}\mathbf{B}\mathbf{R}^T), \quad \forall\mathbf{R} \in \mathsf{SO}(3). \tag{8}$$

As a preliminary step towards the construction of such a function, we need to identify all the invariant quantities. For two second-rank symmetric traceless tensors in three dimensional Euclidean space, there are only eight basic scalars invariant under the full orthogonal group $\mathsf{O}(3)$ [21–24]:

$$\mathcal{I} = \{\mathrm{tr}\mathbf{Q}^2, \mathrm{tr}\mathbf{B}^2, \mathrm{tr}\mathbf{Q}^3, \mathrm{tr}\mathbf{B}^3, \mathrm{tr}\mathbf{Q}\mathbf{B}, \mathrm{tr}\mathbf{Q}^2\mathbf{B}, \mathrm{tr}\mathbf{Q}\mathbf{B}^2, \mathrm{tr}\mathbf{Q}^2\mathbf{B}^2\}, \tag{9}$$

see also [25] for a general reference. Moreover, it is known that the same set of basic invariants forms the minimal monomial basis for the proper rotations group $\mathsf{SO}(3)$ [21–24]. In general, no element in this set can be expressed as a polynomial in the remaining elements and for this reason $\mathcal{I}$ is said to form a *minimal integrity basis*. For $\mathbf{Q}$ and $\mathbf{B}_0$ that share the same eigenframe, the number of basic invariants in $\mathcal{I}$ is reduced to seven by virtue of the identity

$$\mathrm{tr}\mathbf{B}_0^2\mathrm{tr}\mathbf{Q}^2 = 6\mathrm{tr}(\mathbf{Q}^2\mathbf{B}_0^2) - 2(\mathrm{tr}\mathbf{Q}\mathbf{B}_0). \tag{10}$$

Since the two tensors $\mathbf{Q}$ and $\mathbf{B}$ are in general expressed in terms of seven independent variables, as remarked above, then the eight invariants in $\mathcal{I}$ are expected to be only polinomially independent but, functionally, dependent. Actually, a special identity holds [26–29], which is a cubic relation in the invariant $\mathrm{tr}\mathbf{Q}^2\mathbf{B}^2$ and with coefficients depending on the remaining invariants. When the two eigenframes coincide, then the named identity entails the relationship (10) which reduces by one the basic invariants. On the other hand, in this latter case, the number of independent variables describing $\mathbf{Q}$ and $\mathbf{B}_0$ is four and, accordingly, there exist extra functional relations involving the seven basic invariants (see [26,30]). The following development is not affected by them; the minimal integrity basis $\mathcal{I}$ serves to construct a minimal (essential) SO(3)-invariant Landau potential of fourth order. Should an higher order expansion be needed, then the extra functional relations would be useful in reducing the corresponding expansion, but up to the fourth order the monomials in $\mathcal{I}$ are to be regarded as independent.

## 3. GENERAL LANDAU FREE-ENERGY

Traditionally, Landau theories offer a remarkably economic description of phase transitions associated with breaking of some symmetry. They are also intended to be precursors to continuum theories for the description of static order field configurations in non-homogeneous systems by also taking into account for elasticity.

A general Landau-type free-energy for biaxial nematics is a rotationally invariant power-series expansion in the two order tensors around the isotropic phase, that is $\mathbf{Q} = \mathbf{0} = \mathbf{B}$. According to the above minimal integrity basis $\mathcal{I}$, the most general and minimal SO(3)-invariant polynomial up to the fourth order in the two order tensors has 14 terms. It has the form

$$\begin{aligned}\mathcal{G}(\mathbf{Q},\mathbf{B}) = {} & a_1\mathrm{tr}\mathbf{Q}^2 + a_2\mathrm{tr}\mathbf{Q}^3 + a_3(\mathrm{tr}\mathbf{Q}^2)^2 + a_4\mathrm{tr}\mathbf{B}^2 + a_5(\mathrm{tr}\mathbf{B}^2)^2 + a_6\mathrm{tr}\mathbf{Q}\mathbf{B}^2\\ & + a_7\mathrm{tr}\mathbf{Q}^2\mathbf{B}^2 + a_8(\mathrm{tr}\mathbf{Q}\mathbf{B})^2 + a_9\mathrm{tr}\mathbf{Q}\mathbf{B} + a_{10}\mathrm{tr}\mathbf{B}^3 + a_{11}\mathrm{tr}\mathbf{Q}^2\mathbf{B}\\ & + a_{12}\mathrm{tr}\mathbf{Q}^3\mathbf{B} + a_{13}\mathrm{tr}\mathbf{Q}\mathbf{B}^3 + a_{14}\mathrm{tr}\mathbf{Q}^2\mathrm{tr}\mathbf{B}^2\end{aligned} \tag{11}$$

with phenomenological coefficients $a_1, \ldots, a_{14}$. This function represents the most general frame-indifferent bulk free-energy associated with biaxial nematic liquid crystals within the *Landau theory*.

Normally, only the coefficients in front of the quadratic invariants, i.e. $a_1$, $a_4$, and $a_9$, are taken to depend on temperature. This dependence is assumed here to be linear and, moreover, without loss of generality to our purpose, we can assume that only $a_1$ and $a_4$ depend on temperature:

$$a_1 = a_0(t - t^*), \quad a_4 = b_0(t - t_b^*), \quad a_0, b_0 > 0. \tag{12}$$

This is a general plausible assumption. Here $t$ denotes the absolute temperature. The temperature $t^*$ is the *supercooling* temperature of the isotropic phase at the isotropic-to-uniaxial phase transition, while $t_b^*$ is the supercooling temperature of the isotropic phase at the isotropic-to-biaxial phase transition. It is reasonable to assume that there exist both liquid crystalline materials for which $t_b^* < t^*$ and liquid crystalline materials for which $t_b^* \geq t^*$. In materials with $t_b^* < t^*$, the molecular constituents interact in a predominantly uniaxial fashion and no microscopic biaxiality is favored. In materials with $t_b^* > t^*$, molecular interactions are such that a stronger biaxial coupling is favored and, accordingly, the probability of giving rise to a direct, isotropic-to-biaxial phase transition is enhanced, thus preventing the system from traversing an intermediate uniaxial phase.

A classical approach to the study of the free-energy $\mathcal{G}$ requires solving the corresponding equilibrium equations

$$\frac{\partial \mathcal{G}}{\partial \mathbf{Q}} = \mathbf{0} = \frac{\partial \mathcal{G}}{\partial \mathbf{B}}. \tag{13}$$

These are very complicate polynomial tensorial equations and they have been studied completely in specific cases (see [26]). Here, we focus our attention on a necessary equilibrium condition for the pair $(\mathbf{Q}, \mathbf{B})$ which stems from (13) and which requires $\mathcal{G}$ to be stationary with respect to changing $\mathbf{B} \mapsto \mathbf{B}' = \mathbf{R}\mathbf{B}\mathbf{R}^T$. This is a relative equilibrium condition which reads as

$$\begin{aligned} &a_6\left[\mathbf{B}^2, \mathbf{Q}\right] + a_7\left[\mathbf{B}^2, \mathbf{Q}^2\right] + a_{11}\left[\mathbf{B}, \mathbf{Q}^2\right] \\ &+\left(2a_8(\mathrm{tr}\mathbf{Q}\mathbf{B}) + a_9 + \frac{a_{12}}{2}\mathrm{tr}\mathbf{Q}^2 + \frac{a_{13}}{2}\mathrm{tr}\mathbf{B}^2\right)[\mathbf{B}, \mathbf{Q}] = \mathbf{0}. \end{aligned} \tag{14}$$

This equation has the trivial solution $[\mathbf{Q}, \mathbf{B}] = \mathbf{0}$ for any choice of the coefficients $a_k$, which amounts to saying that $\mathbf{Q}$ and $\mathbf{B}$ have a common eigenframe. In other words, it is always possible to assume that the ordered phase has a $D_{2h}$ symmetry like the molecular constituents.

In general, the values of the coefficients $a_k$ can be calculated from a microscopic theory, if it is available, or considered as free parameters in a phenomenological approach. In the paper, we followed a different strategy, that is a semi-phenomenological approach which can be summarized as follows: finding bounds on the coefficients $a_k$ for the free-energy $\mathcal{G}$ to predict a phase diagram consistent with a microscopic model and the type of transitions found experimentally in the last few years [1–6]. However, in general, as a preliminary step, one has to select them and their signs in order to give $\mathcal{G}$ the meaning of an admissible free-energy. One requirement is stability against an unlimited growth of the order tensors; for this, two necessary conditions are

$$a_3 > 0, \quad \text{and} \quad a_5 > 0. \tag{15}$$

Moreover, by setting $\mathbf{B} = \mathbf{0}$ we recover the conventional single-tensor Landau-de Gennes free-energy which describes the transition to the uniaxial phase. For this to happen we need to enforce the requirement

$$a_2 < 0, \quad \text{and} \quad a_3 > 0. \tag{16}$$

The constraints (15) and (16) are general and necessary but they still leave unsolved the problem of the selection of particular numerical values of all the coefficients. Special guidelines are to be employed to determine them completely in order to comply with the above semi-phenomenological criteria.

As mentioned in the Introduction section, experimentally, evidence has been found of first- and second-order transition from the uniaxial ($\mathsf{N_U}$) to the biaxial nematic phase ($\mathsf{N_B}$) and of direct first-order transition from the biaxial phase to the isotropic one. On the side of microscopic models, usually employed in the investigation of biaxial nematic phases, one of the most fruitful has shown to be the quadratic pairwise interaction potential

$$V = -U_0\{\xi\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}'\}, \tag{17}$$

which couples two generic biaxial molecules represented by the tensors $(\mathbf{q},\mathbf{b})$ and $(\mathbf{q}',\mathbf{b}')$. In (17) $U_0$ is a typical interaction energy and $\xi,\gamma,\lambda$ are model parameters constrained by the inequalities

$$\lambda > 0, \quad |2\gamma| < (\xi + \lambda), \tag{18}$$

in order to guarantee a biaxial ground state with perfectly aligned corresponding molecular axes. Over the years, various specific parameterizations have been proposed and studied for (17), based on different grounds and motivations; one of them, due to Straley [15] is based on an approximate mapping from hard-parallelepiped model; another, more often studied one, is $\xi = 1, \lambda = \gamma^2$; this can also be obtained by starting from a dispersion model at the London-de

Boer-Heller approximation [31–33] and isotropically averaging over the orientation of the intermolecular vector (see, e.g. [34,35]). It takes the effective form of Freiser's potential [17,18]

$$V_d = -U_0\epsilon\cdot\epsilon', \quad \epsilon = \mathbf{q}+\gamma\mathbf{b}, \quad \epsilon' = \mathbf{q}'+\gamma\mathbf{b}'. \tag{19}$$

Both the Straley model [15] and the *dispersive* one (19) mostly predict a biaxial-to-uniaxial transition of second-order, followed by a uniaxial-to-isotropic transition of first-order; a direct biaxial-to-isotropic transition of second-order only exists for special values of the potential parameters: $\lambda = \frac{1}{9}, \gamma = \frac{1}{3}$ in (19) (isolated Landau point).

Recently, by using a mean-field approximation, it has been shown that, within the constraints (18), the phase transition diagram predicted by the general potential (17) reveals universal phase sequences [10]. The equilibrium phase sequences predicted by this model are of a limited variety. Upon decreasing temperature $t$, four different equilibrium sequences may take place in adjacent regions of the model parameters; let "$\mathsf{Iso}$" denote the isotropic phase and let "$-$" and "$=$" denote first- and second-order transitions, respectively. Thus, the possible sequences are: $\mathsf{Iso} - \mathsf{N_U} = \mathsf{N_B}, \mathsf{Iso} - \mathsf{N_U} - \mathsf{N_B}, \mathsf{Iso} - \mathsf{N_B}$ and, for singular values of the parameters, $\mathsf{Iso} = \mathsf{N_B}$. In going from the first to the second sequence, a *tricritical point* is to be met along the uniaxial-to-biaxial transition, where the transition reverts from second- to first-order. The second and the third sequences become compatible through a line of *triple points*, where all the phases, $\mathsf{Iso}$, $\mathsf{N_U}$ and $\mathsf{N_B}$ coexist. All these sequences have been also confirmed by Monte Carlo simulation studies [12,14]. The singular set of parameters which leads to all four possible sequences, including $\mathsf{Iso} = \mathsf{N_B}$, is represented by the case $\gamma = 0$ and actually reflects an invariance property that the corresponding interaction potential $V$ enjoys. More precisely, when $\gamma = 0$ the potential reads

$$\begin{aligned} V &= -U_0\{\xi\mathbf{q}\cdot\mathbf{q}' + \lambda\mathbf{b}\cdot\mathbf{b}'\} \qquad (20)\\ &= -U_0\left\{-\left(\lambda+\frac{\xi}{3}\right) + (\xi-\lambda)(\boldsymbol{m}\cdot\boldsymbol{m}')^2 + 2\lambda\left[(\boldsymbol{e}\cdot\boldsymbol{e}')^2 + (\boldsymbol{e}_\perp\cdot\boldsymbol{e}'_\perp)^2\right]\right\}. \qquad (21) \end{aligned}$$

Thus, two simultaneous rotations by $\pm\frac{\pi}{2}$ around the two unit vectors $\boldsymbol{m}$ and $\boldsymbol{m}'$, respectively (i.e. taking place in the individual molecular frames), conserve the potential. This is a consequence of the fact that the mutual coupling between the corresponding lateral molecular arms $(\boldsymbol{e},\boldsymbol{e}')$ and $(\boldsymbol{e}_\perp,\boldsymbol{e}'_\perp)$ is the same; in the group theoretic language this is a $D_{4h}$-invariance of the interaction. Moreover, if one considers a sample of interacting particles (for instance, on a lattice as it happens in Monte Carlo simulation studies) a rotation of each of them by $\pm\frac{\pi}{2}$ around its third axis conserves each pair interaction and hence the overall potential energy. The occurrence of this symmetry, which is broken when $\gamma \neq 0$, causes the appearance of the second-order $\mathsf{Iso} = \mathsf{N_B}$ transition line in the corresponding phase diagram and, accordingly, the additional tricritical point on the transition line between the isotropic and the biaxial phases. On the other hand, the topology of the universal phase diagram for biaxial nematics predicted by the general case $\gamma \neq 0$ is fully reproduced by the symmetric case $\gamma = 0$ as well. Actually, this is also physically reasonable. In the classical uniaxial interaction, just the long axes interact with themselves; if there is any type of interaction between them and the two lateral axes, a good first approximation is that this interaction is the same for both short axes. Thus, the symmetric case embodies the essence of the general biaxial interaction (17), but it also provides the richest structure in the phase diagram. The $D_{4h}$-symmetry transformation can be rephrased in terms of the molecular tensors as follows: when $\gamma = 0$ the pair potential $V$ is invariant under the simultaneous changes $\mathbf{b} \mapsto -\mathbf{b}$ and $\mathbf{b}' \mapsto -\mathbf{b}'$. Accordingly, within a mean-field approximation, the free-energy associated with the symmetric pair potential turns out to be even with respect to $\mathbf{B}$, i.e., invariant with respect to reversion in sign $\mathbf{B} \mapsto -\mathbf{B}$ [26]. This suggests that a Landau free-energy even with respect to $\mathbf{B} \mapsto -\mathbf{B}$ and chosen within the general class represented by $\mathcal{G}$, may be sufficiently general to reproduce the universal phase diagram of biaxial nematics. Therefore, we shall introduce and focus our attention on such a free-energy and we shall also present the phase diagram it is capable of predicting.

## 3.1. Symmetric Landau Potential

Up to fourth order, the general Landau potential consists of fourteen invariant terms. Here we focus our attention on a class of models which enjoy the additional $D_{4h}$-symmetry property. As remarked above, this symmetry is a consequence of letting $\gamma = 0$ in (17). Thus, we require the Landau potential to be invariant under the transformation $(\mathbf{Q}, \mathbf{B}) \mapsto (\mathbf{Q}, -\mathbf{B})$ so that $\mathcal{G}$ reduces to

$$\begin{aligned}\mathcal{F}(\mathbf{Q}, \mathbf{B}) = {}& a_1 \mathrm{tr}\mathbf{Q}^2 + a_2 \mathrm{tr}\mathbf{Q}^3 + a_3\left(\mathrm{tr}\mathbf{Q}^2\right)^2 + a_4 \mathrm{tr}\mathbf{B}^2 + a_5\left(\mathrm{tr}\mathbf{B}^2\right)^2 + a_6 \mathrm{tr}\mathbf{Q}\mathbf{B}^2 \\ & + a_7 \mathrm{tr}\mathbf{Q}^2\mathbf{B}^2 + a_8(\mathrm{tr}\mathbf{Q}\mathbf{B})^2 + a_{14} \mathrm{tr}\mathbf{Q}^2 \mathrm{tr}\mathbf{B}^2. \qquad (22)\end{aligned}$$

In order to shape the corresponding phase diagram, so that it can comply with the universal phase sequences described above, we need to find suitable bounds on the nine coefficients appearing in $\mathcal{F}$. First of all, we restrain the class of tensors minimizing $\mathcal{F}$ to those ones sharing the same eigenframe. As shown above, this is always the case for any choice of the coefficients. Secondly, we further restrain the critical points of $\mathcal{F}$ by requiring them to comply with the symmetry $\mathcal{F}(\mathbf{Q},\mathbf{B})=\mathcal{F}(\mathbf{Q},-\mathbf{B})$. In particular, we assume that any tensorial macroscopic observable $\mathbf{A}=\alpha\mathbf{Q}+\beta\mathbf{B}$ resulting from the ensemble average of a microscopic observable $\boldsymbol{a}=\alpha\mathbf{q}+\beta\mathbf{b}$, with $\alpha$ and $\beta$ scalars, have the same spectrum as the tensorial macroscopic observable $\mathbf{A}^*=\alpha\mathbf{Q}-\beta\mathbf{B}$ resulting from the ensemble average of $\mathbf{a}^*=\alpha\mathbf{q}-\beta\mathbf{b}$. According to this criterion, stated in [10,26], this is equivalent to subjecting the two tensors to the constraints

$$\mathrm{tr}\mathbf{B}^3=0,\quad \mathrm{tr}\mathbf{B}\mathbf{Q}^2,\quad \mathrm{tr}\mathbf{Q}\mathbf{B}=0, \tag{23}$$

which, combined with the assumption of common eigenframe, leads to the following effective tensors, minimizing $\mathcal{F}$,

$$\widetilde{\mathbf{Q}}=S\left(\boldsymbol{e}_z\otimes\boldsymbol{e}_z-\frac{1}{3}\mathbf{I}\right),\quad \widetilde{\mathbf{B}}_0=T'\big(\boldsymbol{e}_x\otimes\boldsymbol{e}_x-\boldsymbol{e}_y\otimes\boldsymbol{e}_y\big). \tag{24}$$

Given these restraining criteria, it is then quite natural to quest for stability around the corresponding critical points (24) against fluctuations in the silent order parameters $S'$ and $T$ and against distortions which tend to disalign the coinciding eigenframes, whichever the choice of $\widetilde{\mathbf{Q}}$ and $\widetilde{\mathbf{B}_0}$ is. Provided that $S>0$, i.e., only calamitic uniaxial states are allowed (in line with the above universal sequences), this stability criterion leads to the constitutive inequalities (see [26])

$$a_6>0,\quad a_7>0,\quad a_8\geq-\frac{1}{3}a_7. \tag{25}$$

A reduced effective free-energy is thus obtained

$$\begin{aligned}\mathcal{F}_0(S,T'):=\mathcal{F}(S,0,0,T')&=\frac{2}{3}a_1S^2+\frac{2}{9}a_2S^3+\frac{4}{9}a_3S^4+2a_4T'^2\\&\quad+4a_5T'^4-\frac{2}{3}a_6ST'^2+\frac{2}{9}a_7'S^2T'^2.\end{aligned} \tag{26}$$

A detailed analysis of (26) performed in [26] which includes stability analysis in $S$ and $T'$, bifurcation analysis of the corresponding equilibrium equations, study of tricriticality and computation of transition lines, allows one to construct the phase diagram represented in Figure 1. Since only $a_1$ and $a_4$ are taken to depend on temperature, then it makes sense to represent the thermal behaviour onto the $(a_4,a_1)$-plane. In Figure 1 the straight lines are parameterized

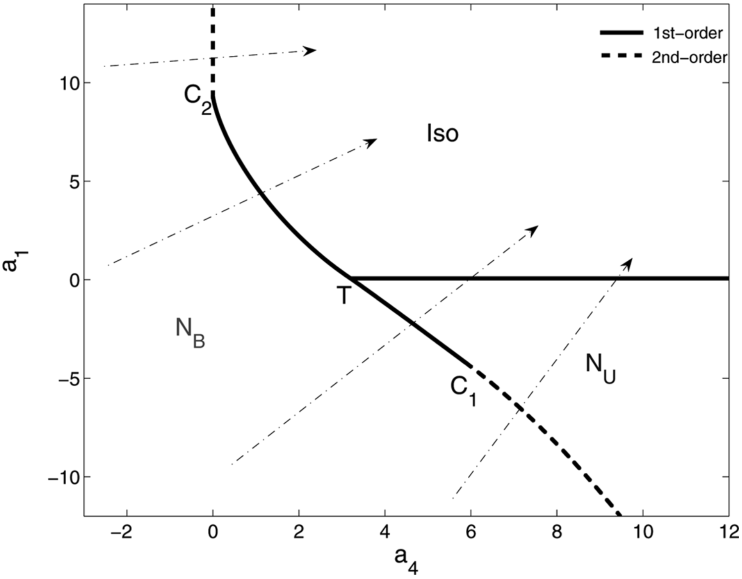

**FIGURE 1.** (Color online) The phase transition diagram predicted by the free-energy $\mathcal{F}$ in (22) when the coefficients are selected as in (29). The free-energy $\mathcal{F}$ is able to capture both second- and first-order transitions between the isotropic (Iso) and biaxial phases ($N_B$) and between the uniaxial ($N_U$) and biaxial phases, with the appearance of two tricritical points, $C_1$ and $C_2$. The transition between the isotropic and uniaxial phases remains first-order for all parameters chosen according to (29). T is the triple point where the isotropic, uniaxial, and biaxial phases coexist in equilibrium. The arrows represent temperature axes with temperature increasing in the direction of the arrows. These straight lines are parameterized by the phenomenological coefficients $a_0$ and $b_0$ and by the difference $\Delta$ between the two supercooling temperatures $t^*$ and $t_b^*$, see (28) and (27).

by the equation

$$a_4 = \left(\frac{b_0}{a_0}\right) a_1 + b_0 \Delta, \tag{27}$$

where

$$\Delta := t^* - t_b^*. \tag{28}$$

They represent the thermal lines, i.e., along them the temperature increases in the direction of the corresponding arrows. According to our choice of the phenomenological coefficients $a_0, b_0, t_b^*, t^*$, we recover all possible sequences of phase predicted within the microscopic theory governed by the pair potential in (17) and the type of transitions which seem to have been found experimentally. The specific topology of the phase diagram in Figure 1 is not ensured for any choice of the phenomenological coefficients $a_k$. It is natural to pose the question of existence of minimal and, to some extent, optimal conditions on $a_k$ in order to obtain all the thermodynamical properties illustrated above. These thermodynamical properties directly yield topological properties in the two-dimensional phase diagram coordinated by $a_4, a_1$. Therefore, these conditions should make the phase diagram topologically stable for all free-energies in the class (22). Some of these conditions are general and have been already illustrated (see (15), (16) and (25)). Additionally, we have to guarantee specific properties which are:

(i) Existence of the $\mathsf{N_U} = \mathsf{N_B}$ transition for arbitrary calamitic uniaxial order parameters;
(ii) Existence of tricritical points appropriately separated by first- and second-order transition lines;
(iii) Existence of well-separated triple and tricritical points.

All these requirements are fullfilled provided that the following constitutive inequalities hold, which also include those ones found above (see details in [26])

$$a_2 < 0, \quad a_3 > 0, \quad \frac{(a_7 + 6a_{14})^2}{144a_3} < a_5 < \frac{a_6^2 a_3}{a_2^2},$$
$$a_6 > 0, \quad 0 < a_7 \le -6a_{14}, \quad a_8 \ge -\frac{1}{3}a_7. \qquad (29)$$

These conditions are quite general and not too restrictive. They ensure that in the absence of external distorting causes, the most general phase diagram associated with the symmetric Landau potential $\mathcal{F}$ is the one illustrated in Figure 1.

## 3.2. Comparison with Other Landau Models

Other phenomenological potentials for biaxial liquid crystals have already been proposed in the past. We briefly signal in what our approach differs from the ones already taken in the literature. The other proposed theories may be classified according to the number $\mathfrak{t}$ of order tensors employed to describe the condensed phases and the highest degree $\mathfrak{g}$ at which a single scalar order parameter enters the polynomial potential. Thus, in [36] $\mathfrak{t} = 2$ and $\mathfrak{g} = 6$, while in [16,36] $\mathfrak{t} = 1$ and $\mathfrak{g} = 6$, and in [38] $\mathfrak{t} = 2$ and $\mathfrak{g} = 18$; by contrast, in our theory $\mathfrak{t} = 2$ and $\mathfrak{g} = 4$. A somewhat intermediate scenario is offered by [39] and [40]. In [39], the uniaxial and biaxial components of $\mathbf{Q}$ are treated independently in the free-energy and the corresponding scalar order parameters, $S$ and $T$ in our language, appear at the most in the sixth degree. The phenomenological theory of [40] is phrased in terms of two order tensors, the analogs of our $\mathbf{Q}$ and $\mathbf{B}$, but $\mathbf{B}$ is expressed as a function of $\mathbf{Q}$ in the vicinity of the uniaxial-to-biaxial transition, by use of the equilibrium equations evaluated along the bifurcating biaxial branch; as a consequence of this procedure it turns out that $\mathbf{B} \sim \mathbf{Q}^2$ and the free-energy is thus reduced to a polynomial potential of degree six in the scalar order parameters of $\mathbf{Q}$. The reduced theory reads

$$\mathcal{W} = a\,\mathrm{tr}\mathbf{Q}^2 + b\,\mathrm{tr}\mathbf{Q}^3 + c(\mathrm{tr}\mathbf{Q}^2)^2 + d\,\mathrm{tr}\mathbf{Q}^2\mathrm{tr}\mathbf{Q}^3 + e(\mathrm{tr}\mathbf{Q}^2)^3 + f(\mathrm{tr}\mathbf{Q}^3)^2 \tag{30}$$

and it has been carefully re-examined in [41]. Actually, as remarked above, a very first analysis of this free-energy had been already performed in [16,42] and a singular phase diagram had been found which reproduced the same topology as the one predicted by the microscopic theory (19).

Instead in [41], according to the choice of the coefficients in (30), several possible scenarios have been identified and classified. Here $a$ is taken to depend linearly on $t$ as well as the coefficient $a_1$ in $\mathcal{F}$ and $\mathcal{G}$. According to [41], by choosing the $(a, b)$-plane representation, *ten* qualitatively different topologies of phase diagram have been shown to be predicted by the free-energy $\mathcal{W}$. The type of transitions predicted can be first- and second-order from the uniaxial to the biaxial phase, first-order direct between the isotropic and the biaxial phases and from the isotropic to the uniaxial one; thus, triple and tricritical points have been found. However, none of the ten cases reproduces entirely the phase diagram in Figure 1. In particular, what is missing is the line of second-order phase transitions from the isotropic to the biaxial phase and the corresponding tricritical point ($\mathsf{C}_2$ in Fig. 1). A possible explanation is that in the reduced theory (30) the tensor $\mathbf{B}$ is assumed to be a function of $\mathbf{Q}$ at the equilibrium, but this is not always the case. Actually, here we are treating the two order tensors on the same footing, as it is also clear from the assumption of the existence of two supercooling temperatures: one, $t^*$, related to the onset of a uniaxial or biaxial phase guided by $\mathbf{Q}$ and the other, $t_b^*$, related to the possible onset from the isotropic phase of a biaxial phase led by $\mathbf{B}$. According to the choice of the free phenomenological coefficients, one of the two mechanisms or the other can become predominant, and, moreover, they can lead to special features of the phase diagram.

Furthermore, another important difference between all the other theories and ours is that the former suffer from a great number of phenomenological coefficients rivalling with the number of topologically different phase diagrams they may predict. The approach we attempted here went somehow in the opposite direction, seeking guidance in a molecular model to restrain the variety of phase diagrams and, consequently, to reduce both number and range of the admissible phenomenological coefficients.

## 4. ELASTICITY

Positing a continuum theory for biaxial nematics requires the addition of gradient terms in $\mathbf{Q}$ and $\mathbf{B}$ to $\mathcal{G}$ or $\mathcal{F}$. The free-energy $\mathcal{G}$ describes the homogeneous alignment in the liquid crystals. For non-homogeneous systems spatial deformations are important, especially in confined geometries, such as display devices. Actually, there are signs of biaxiality in the uniaxial phase when the nematic is subject to large strain, as in the case, close to defects. The tendency of the liquid crystal to resist any deformation, its curvature elasticity, can be accounted for by including terms in the gradients of the order tensors in the free-energy. Let $\mathcal{B}$ be a bounded, open, connected subset of $\mathbb{R}^3$, with boundary $\partial\mathcal{B}$. Physically speaking, $\mathcal{B}$ represents the region of confinement of a liquid crystal. Let $x := (x_1, x_2, x_3) \in \mathcal{B} \subset \mathbb{R}^3$, and let $\mathbf{Q}(\boldsymbol{x})$, $\mathbf{B}(\boldsymbol{x})$ be now two symmetric, second-rank tensor fields having zero trace. In a similar way to the usual practice for uniaxial nematics, we consider terms that are quadratic in the gradients $\nabla\mathbf{Q}$ and $\nabla\mathbf{B}$. Thus, the most general elastic free-energy density turns out to be

$$\begin{aligned}\mathcal{G}_{el}(\nabla\mathbf{Q}, \nabla\mathbf{B}) := & L_1 Q_{ij,k} Q_{ij,k} + L_2 Q_{ij,j} Q_{ik,k} + L_3 Q_{ij,k} Q_{ik,j} \\ & + M_1 B_{ij,k} B_{ij,k} + M_2 B_{ij,j} B_{ik,k} + M_3 B_{ij,k} B_{ik,j} \\ & + 2N_1 Q_{ij,k} B_{ij,k} + 2N_2 Q_{ij,j} B_{ik,k} + 2N_3 Q_{ij,k} B_{ik,j}, \qquad (31)\end{aligned}$$

where $L_1, L_2, L_3, M_1, M_2, M_3, N_1, N_2, N_3$ are material *elastic constants* and $Q_{ij,k} = \frac{\partial Q_{ij}}{\partial x_k}$, $B_{ij,k} = \frac{\partial B_{ij}}{\partial x_k}$. Summation over repeated indices is assumed. Hence, in general, there are 9 elastic constants. In general, the problem of the minimal number of terms and, accordingly, the minimal number of elastic constants is a matter of debate. Here, we take as a first approximation, the following reduced expression

$$\mathcal{G}_{el}(\nabla\mathbf{Q}, \nabla\mathbf{B}) := l_1|\nabla\mathbf{Q}|^2 + 2l_2\nabla\mathbf{Q}\cdot\nabla\mathbf{B} + l_3|\nabla\mathbf{B}|^2, \tag{32}$$

where $\nabla\mathbf{Q}\cdot\nabla\mathbf{B} = Q_{ij,k}B_{ij,k}$ and $|\nabla\mathbf{Q}|^2 = \nabla\mathbf{Q}\cdot\nabla\mathbf{Q}$. Only 3 elastic constants are present in (32) and they are such that $l_1 > 0$, $l_1l_3 - l_2^2 > 0$ for the elastic free-energy density $\mathcal{G}_{el}$ to be positive-definite.

As a consequence, as far as the statics of the biaxial nematic liquid crystal is concerned, one should consider in general the free-energy density given by the sum of the two contributions above: the bulk free-energy (Landau potential) $\mathcal{G}$ and the elasticity term $\mathcal{G}_{el}$, thus obtaining the volumetric *Landau-Ginzburgh free-energy functional* for a liquid crystal confined in a bounded, open, connected subset $\mathcal{B}$ of $\mathbb{R}^3$

$$\mathfrak{F} := \int_{\mathcal{B}}\{\mathcal{G}(\mathbf{Q},\mathbf{B}) + \mathcal{G}_{el}(\nabla\mathbf{Q},\nabla\mathbf{B})\}. \tag{33}$$

The bulk potential $\mathcal{G}$ inhibits departures of $\mathbf{Q}$ and $\mathbf{B}$ from the preferred uniaxial or biaxial states (according to the value of the working temperature) and its preferred degree of orientational order and, moreover, from the configuration with common eigenframe $(\mathbf{Q}, \mathbf{B}_0)$. The elastic energy $\mathcal{G}_{el}$ penalizes distortions in space of the eigenframes of both $\mathbf{Q}$ and $\mathbf{B}$ and their relative orientation and spatial variations in the degree of order. Surface terms should be in general included for a complete description of confined liquid crystals. Thus, the full free-energy functional has to be provided with the integral over the boundary $\partial\mathcal{B}$ of a *surface* free-energy density $\mathcal{G}_s(\mathbf{Q},\mathbf{B})$, i.e.,

$$\mathfrak{F} = \int_{\mathcal{B}}\{\mathcal{G}(\mathbf{Q},\mathbf{B}) + \mathcal{G}_{el}(\nabla\mathbf{Q},\nabla\mathbf{B})\} + \int_{\partial\mathcal{B}}\mathcal{G}_s(\mathbf{Q},\mathbf{B}). \tag{34}$$

Moreover, sometimes, it is also necessary to introduce a further contribution $\mathfrak{F}_L$ to $\mathfrak{F}$ which usually is linear in $\mathbf{Q}$ and $\mathbf{B}$. It contains effects that couple linearly to $\mathbf{Q}$ and $\mathbf{B}$, e.g., the free-energy density due to an externally applied magnetic or electric field, the linear part of a surface potential, etc. A typical form would be

$$\mathfrak{F}_L = \int_{\mathcal{B}}\{\mathrm{tr}(\mathbf{HQ}) + \mathrm{tr}(\mathbf{EB})\} + \int_{\partial\mathcal{B}}\{\mathrm{tr}(\mathbf{H_sQ}) + \mathrm{tr}(\mathbf{E_sB})\}. \tag{35}$$

The resulting Landau–Ginzburgh free-energy has to be minimized to find equilibrium configurations: this can be accomplished by solving the associated Euler-Lagrange equations. We shall propose, in the next subsection, a simplified model and we shall present the corresponding equilibrium equations.

### 4.1. Symmetric Ginzburgh–Landau Free-Energy Density

Inspired by the symmetry argument used for the reduction of the Landau potential $\mathcal{G}$, we now propose a simplified model which treats on the same footing the bulk and the elasticity contributions. We introduce the free-energy density

$$\mathcal{H}(\mathbf{Q},\mathbf{B},\nabla\mathbf{Q},\nabla\mathbf{B}) := \mathcal{F}(\mathbf{Q},\mathbf{B}) + \frac{l_Q}{2}|\nabla\mathbf{Q}|^2 + \frac{l_B}{2}|\nabla\mathbf{B}|^2, \quad l_Q > 0, l_B > 0, \tag{36}$$

which turns out to be symmetric with respect to the transformation $(\mathbf{Q}(\boldsymbol{x}),\mathbf{B}(\boldsymbol{x})) \mapsto (\mathbf{Q}(\boldsymbol{x}),-\mathbf{B}(\boldsymbol{x}))$ for all $\boldsymbol{x} \in \mathcal{B}$. The symmetric Landau potential $\mathcal{F}$ inhibits departures of $\mathbf{Q}$ and $\mathbf{B}$ from the homogeneous phases described by $\widetilde{\mathbf{Q}}$ and $\widetilde{\mathbf{B}}_0$ in (24). The two quadratic terms in the gradients of $\mathbf{Q}$ and $\mathbf{B}$ penalize distortions in space of the eigenframes of both $\mathbf{Q}$ and $\mathbf{B}$ and spatial variations in the degree of order. When $\mathbf{Q}$ and $\mathbf{B}$ are prescribed on $\partial\mathcal{B}$, the equilibrium equations for the two order tensor fields $\mathbf{Q}(\boldsymbol{x})$ and $\mathbf{B}(\boldsymbol{x})$ are the following

$$\frac{\partial\mathcal{F}}{\partial\mathbf{Q}} - l_Q\Delta\mathbf{Q} = \mathbf{0}, \tag{37}$$

$$\frac{\partial\mathcal{F}}{\partial\mathbf{B}} - l_B\Delta\mathbf{B} = \mathbf{0}, \tag{38}$$

or, more precisely,

$$\begin{aligned} l_Q\Delta\mathbf{Q} = &-\left(a_2\mathrm{tr}\mathbf{Q}^2 + \frac{1}{3}a_6\mathrm{tr}\mathbf{B}^2 + \frac{2}{3}a_7\mathrm{tr}\mathbf{Q}\mathbf{B}^2\right)\mathbf{I} + 2(a_1 + 2a_3\mathrm{tr}\mathbf{Q}^2 + a_{14}\mathrm{tr}\mathbf{B}^2)\mathbf{Q} \\ &+ 2a_8(\mathrm{tr}\mathbf{Q}\mathbf{B})\mathbf{B} + 3a_2\mathbf{Q}^2 + a_6\mathbf{B}^2 + a_7(\mathbf{Q}\mathbf{B}^2 + \mathbf{B}^2\mathbf{Q}), \end{aligned} \tag{39}$$

$$\begin{aligned} l_B\Delta\mathbf{B} = &-\frac{2}{3}(a_7\mathrm{tr}\mathbf{B}\mathbf{Q}^2 + a_6\mathrm{tr}\mathbf{Q}\mathbf{B})\mathbf{I} + 2(a_4 + 2a_5\mathrm{tr}\mathbf{B}^2 + a_{14}\mathrm{tr}\mathbf{Q}^2)\mathbf{B} \\ &+ 2a_8(\mathrm{tr}\mathbf{Q}\mathbf{B})\mathbf{Q} + a_6(\mathbf{Q}\mathbf{B} + \mathbf{B}\mathbf{Q}) + a_7(\mathbf{B}\mathbf{Q}^2 + \mathbf{Q}^2\mathbf{B}), \end{aligned} \tag{40}$$

where $\Delta = \sum_{j=1}^{3}\frac{\partial^2}{\partial x_j^2}$. These equations are non-linear coupled partial differential equations for $\mathbf{Q}$ and $\mathbf{B}$ and need to be solved in order to search for equilibrium field configurations in $\mathcal{B}$. Alternatively, one could also keep the symmetric free-energy density $\mathcal{F}$ as bulk contribution and add $\mathcal{G}_{el}$ as in (32) to account for spatial deformations. In this case the symmetry enjoyed by $\mathcal{F}$ would be broken only by elasticity effects. All this pertains to future work.

## 5. CONCLUSIONS AND PERSPECTIVES

We proposed a phenomenological model to describe the full variety of equilibrium phases predicted by a molecular model for biaxial nematics [8,10,12]. Our strategy was inspired by the desire of reducing the number of terms allowed only by symmetry and invariance in the fourth-degree polynomial expansion $\mathcal{G}$ in the order tensors $\mathbf{Q}$ and $\mathbf{B}$, in (11). The potential $\mathcal{G}$ contains fourteen terms invariant under rotations. Guided by the molecular pair potential (17), we reduced the general model to a simpler one, represented by the potential $\mathcal{F}$ in (22), which is symmetric under the change of $\mathbf{B}$ into $-\mathbf{B}$ and contains only nine invariants. This choice was suggested by the qualitative coincidence between the mean-field phase diagram derived in [8] for the special case of the biaxial pair potential (17) with $\gamma = 0$ and the phase diagram obtained in [10] for the most general potential of the form (17). Since all qualitative features of the general phase diagram are already exhibited by the one associated with the pair potential symmetric under the microscopic transformation $\mathbf{b} \mapsto -\mathbf{b}$, we required $\mathcal{G}(\mathbf{Q}, \mathbf{B})$ to be invariant under the macroscopic transformation $\mathbf{B} \mapsto -\mathbf{B}$. Such an invariance requirement was further strengthened and applied to the spectrum of all observables expressed as linear combinations of $\mathbf{Q}$ and $\mathbf{B}$. In particular, requiring this property to be valid at all critical points of $\mathcal{F}$, we eventually reduced to two the number of independent scalar order parameters needed to represent $\mathbf{Q}$ and $\mathbf{B}$ at equilibrium in one and the same eigenframe. Of these two, one belongs to $\mathbf{Q}$ and the other to $\mathbf{B}$; thus, the former tensor is necessarily uniaxial, if not zero, whereas the other is necessarily biaxial, if not zero. The critical points of the potential $\mathcal{F}$ so restrained are the same as those of the restrained potential $\mathcal{F}_0$ in (26), which were subject to a two-fold stability analysis, against relative distorsions of the tensors' eigenframes and against perturbations in the silent scalar order parameters. This analysis, which resulted in restrictions for the admissible phenomenological coefficients of $\mathcal{F}$, ensured that the critical points of $\mathcal{F}_0$ are stable relative to the restraining criteria that reduced $\mathcal{F}$ to $\mathcal{F}_0$. Moreover, extra minimal conditions on the phenomenological coefficients were determined to guarantee the topological stability of the phase diagram represented in Figure 1, which embodies all qualitative features of the universal phase diagram for the molecular theory based on the most general pair potential (17).

The phenomenological potential we propose to describe biaxial phases is $\mathcal{F}$, which in its general formulation (22) is also applicable to order tensors $\mathbf{Q}$ and $\mathbf{B}$ with different eigenframes, each possibly bearing two non-vanishing scalar order parameters, in consequence of an external distorting cause, such as an electric or magnetic field, or in consequence of internal elastic distortions. Whenever the restrictions on the phenomenological coefficients listed in (29) are satisfied, the potential $\mathcal{F}$ reproduces all the desired macroscopic features that our general molecular model [10] attributed to the biaxial pair potential (17). A precise and detailed comparison with experimental data is currently highly desirable in order to set the numerical values of the coefficients $a_k$ within the bounds (29) according to specific molecular systems.

We also put forward a general Ginzburgh–Landau model for non-homogeneous systems in confined geometries. A simplified form ($\mathcal{H}$ in (36)) of the corresponding free-energy density has been proposed as well. It includes the potential $\mathcal{F}$ as bulk contribution and gradient terms invariant under the same symmetry transformation ($\mathbf{B} - > -\mathbf{B}$) as in $\mathcal{F}$. The associated equilibrium equations have been presented and left for future investigations. We also plan to form a complete dynamic theory which also accounts for dissipation [43].

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