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Minimal coupling model of the biaxial nematic phase

Lech Longa*
Marian Smoluchowski Institute of Physics, Department of Statistical Physics and Mark Kac Complex Systems Research Center, Jagiellonian University, Reymonta 4, Kraków, Poland

Piotr Grzybowski
Marian Smoluchowski Institute of Physics, Department of Statistical Physics, Jagiellonian University, Reymonta 4, Kraków, Poland

Silvano Romano
Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica "A. Volta," Università di Pavia, via A. Bassi 6, I-27100 Pavia, Italy

Epifanio Virga
Istituto Nazionale per la Fisica della Materia e Dipartimento di Matematica "F. Casorati," Università di Pavia, via A. Ferrata 1, I-27100 Pavia, Italy

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A minimal coupling model exhibiting isotropic, uniaxial, and biaxial nematic phases is analyzed in detail and its relation to existing models known in the literature is clarified. Its intrinsic symmetry properties are exploited to restrict the relevant ranges of coupling constants. Further on, properties of the model are thoroughly investigated by means of bifurcation theory as proposed by Kayser and Raveché [Phys. Rev. A **17**, 2067 (1978)] and Mulder [Phys. Rev. A **39**, 360 (1989)]. As a first step toward this goal, the bifurcation theory is applied to a general formulation of density functional theory in terms of direct correlation functions. On a general formal level, the theory is then analyzed to show that the bifurcation points from the reference, high-symmetry equilibrium phase to a low-symmetry structure depend only on the properties of the one-particle distribution function and the direct pair correlation function of the reference phase. The character of the bifurcation (whether spinodal, critical, tricritical, isolated Landau point, etc.) depends, in addition, on a few higher-order direct correlation functions. Explicit analytical results are derived for the case when only the leading $L=2$ terms of the potential (mean-field analysis) or of the direct pair correlation function expansion in the symmetry-adapted basis are retained. Formulas are compared with the numerical calculations for the mean-field, momentum $L=2$ potential model, in which case they are exact. In particular, bifurcations from the isotropic and uniaxial nematic to the biaxial nematic phases are discussed. The possibility of the recently reported nematic uniaxial–nematic biaxial tricritical point [A. M. Sonnet, E. G. Virga, and G. E. Durand, Phys. Rev. E **67**, 061701 (2003)] is analyzed as well.

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I. INTRODUCTION

Mesogenic materials exhibit a rich variety of liquid-crystalline phases [1]. The simplest of them is the uniaxial nematic, which results in the definition of a single macroscopic Goldstone variable known as the director.

Actually, nematogenic molecules do not possess cylindrical symmetry, and sometimes have appreciable dipole moments, yet the resulting thermotropic mesophases of low-molecular-weight compounds are usually uniaxial and apolar. In a number of cases, theoretical treatments have been (and still are) fruitfully simplified by assuming from the start that nematogenic molecules are $D_{\infty h}$ symmetric. On the the other hand, over the last 30 years, the possible effects of molecular biaxiality (i.e., of deviations from cylindrical symmetry) on nematic order have been studied theoretically as well. Molecular field (MF) [2–12] as well as Landau treatments [13–15], and later simulation studies of lattice models [16–21], have shown that single-component models consisting of molecules possessing D_{2h} symmetry, and interacting by appropriately chosen continuous potentials, can produce a biaxial phase. A similar scenario has emerged from the analytical study of single-component systems consisting of biaxial molecules interacting via hard-core potentials [22–30], also supported by simulation results [31–33]. In both cases, the transition between biaxial and uniaxial nematic phases is mostly found to be second order (but see a partly different scenario in Ref. [12]), and a direct transition between isotropic and biaxial nematic phases is predicted as well. Gay-Berne potential models (see Ref. [34] for a review), originally developed for uniaxial molecules, have been extensively investigated; more recently, biaxial extensions of them have been proposed and studied by simulation (see, e.g., Refs. [35–40]). Most of the above cases involve single-site models possessing D_{2h} symmetry; on the other hand, in a few other cases [30,33], the potential model involves two

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*Present address: Liquid Crystal Institute, Kent State University, POB 5190, Kent OH 44242-0001, USA. Electronic address: lech@alek.if.uj.edu.pl identical interacting moieties in each particle: each of them is uniaxial, and they are connected in a V-shaped fashion. Rigid-molecule models have been considered in the above references, and in some other cases [41] a more general MF treatment was developed, allowing for internal (torsional) degrees of freedom.

On the experimental side, a biaxial phase was discovered in a lyotropic system in 1980 [42]. Since 1986 there have been numerous reports of thermotropic biaxiality in low-molecular-weight compounds (see, e.g., Refs. [43–46]), many of which have since been called into question [47–50]. Only recent experiments on systems involving “banana-shaped” mesogens [51–54] seem finally to provide strong evidence of thermotropic biaxial nematic behavior.

On the theoretical side interest in studying biaxial nematic phase also has increased over the last two years [12,55–57]. In particular, Sonnet *et al.* [12] have proposed a MF model involving only two scalar order parameters (instead of the usual four; see the above references), and exhibiting isotropic and uniaxial and biaxial nematic phases. An interesting feature of the calculated phase diagram is the presence of a tricritical point separating uniaxial and biaxial nematic phases. The MF phase diagram resembles that of McMillan [1,58] for the nematic–to–smectic-A transition.

In this paper we generalize the analysis presented in [12]. In particular we study in detail a microscopic, momentum $L=2$ model for the biaxial nematic phase [6,16] by referring to density functional formulation of the Helmholtz free energy. We start with the derivation of the bifurcation point from the uniaxial to the biaxial nematic phase and determine conditions under which it could change from first to second order. A purpose of this formal analysis is to find a criterion that is thermodynamically exact and shows at what level approximations enter. The formulas will then be illustrated with a MF discussion of the momentum $L=2$ model. Some limiting cases of this model have already been introduced in the literature but no complete MF analysis even for this simplest case has been offered. The phase behavior of the model will be analyzed by exploring its duality properties as well as by bifurcation analysis.

One of the objectives of our analysis is to study thermodynamic and symmetry properties of the simplest model showing a biaxial nematic phase. The model could be helpful to shed light on possible reasons as to why the biaxial nematic is so elusive, especially in thermotropic materials.

This paper is organized as follows. After a detailed discussion of the density functional theory in Sec. II, we utilize the formulation proposed by Mulder [24] to derive general formulas for the uniaxial-to-biaxial nematic bifurcation point. The formulas derived will bring information on whether the bifurcation point is critical, spinodal, or tricritical.

Then in Sec. III we apply the formalism to discuss MF properties of the most general nearest neighbor lattice model with $L=2$ terms, which describes the uniaxial and biaxial phases, and for which the present theory is exact. First, we will discuss a connection of the model with other soft-potential models known from the literature, especially in the context of various parametrizations used by the authors. Next, we will concentrate on (tri)critical properties of the model and show that the two-tensor model [12] is a special case. Our analysis will be exact for a more general case when the symmetry-adapted expansion of the direct pair correlation function is dropped at the lowest relevant order with $L=2$ and when the triplet and higher direct correlations are disregarded.

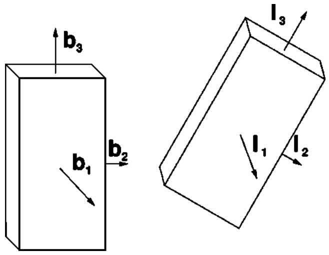

FIG. 1. Orthonormal, right-handed, body-fixed tripods of vectors representing molecular orientations and used to parametrize intermolecular interactions.

II. DENSITY FUNCTIONAL AND BIFURCATION ANALYSIS

We consider a one-component anisotropic fluid, composed of classical, identical, biaxial molecules, interacting through a pairwise additive potential $W(\mathbf{x}_1-\mathbf{x}_2,\mathbf{\Omega}_1,\mathbf{\Omega}_2)$; here the $\mathbf{x}$’s are the positions of the molecular centers of mass and the $\mathbf{\Omega}$’s refer to their orientations. The two molecular orientations can be defined by ordered triplets of Euler angles $\{\phi_j,\theta_j,\psi_j\}$; on the other hand, it also proves convenient to express them in terms of two orthonormal tripods of vectors (e.g., eigenvectors of the two inertia tensors; see Fig. 1), hereafter denoted by $\{\mathbf{b}_i\}$ and $\{\boldsymbol{l}_k\}$, respectively. Intermolecular vectors are defined by

$$\mathbf{r}=\mathbf{x}_1-\mathbf{x}_2, \quad r=|\mathbf{r}|, \quad \hat{\mathbf{r}}=\mathbf{r}/r. \tag{1}$$

The symmetry properties and expansion of the pair potential will be taken up again in the following section. According to density functional theory [59], the grand potential $\Xi[\rho]$ of liquid crystals is a functional of the orientational, one-particle distribution function $\rho(\mathbf{\Omega},\mathbf{x})\equiv\rho(q)$. In the absence of an external field the expression for $\Xi[\rho]$ reads

$$\Xi[\rho]=k_BT\int\rho(q)\{\ln[\Lambda\rho(q)]-1\}dq-\mu\int\rho(q)dq+\mathcal{F}_{\mathrm{ex}}[\rho]. \tag{2}$$

The first term in Eq. (2) represents the ideal-gas contribution with $\Lambda=\sqrt{h^{12}\beta^6/(2\pi)^6m^3I_1I_2I_3}$ resulting from the integration over momenta, where I_1, I_2, and I_3 are the principal moments of inertia, m is the mass, $\beta=1/k_BT$, h is the Planck constant, T is the absolute temperature, and k_B is the Boltzmann constant. $\mathcal{F}_{\mathrm{ex}}[\rho]$ is the excess Helmholtz free energy due to interactions and μ is the chemical potential. Also $\int dq\,\rho(q)\equiv\int d\mathbf{x}\,d\mathbf{\Omega}\,\rho(\mathbf{x},\mathbf{\Omega})=\langle N\rangle$ with $\langle N\rangle$ being the average number of particles in the system. For a given functional form of $\mathcal{F}_{\mathrm{ex}}[\rho]$ the equilibrium one-particle density of the bulk system is found from the variational minimum of Ξ

with respect to ρ. The necessary condition yielding a stationary distribution $\rho_S(q)$ reads

$$\left.\frac{\delta\Xi[\rho]}{\delta\rho}\right|_{\rho=\rho_S} = k_BT\ln\Lambda + k_BT\ln\rho_S(q) - \mu - k_BTC_1(q,[\rho_S]) = 0, \tag{3}$$

for fixed value of μ. Note that μ also serves as a Lagrange multiplier to guarantee that normalization of $\rho_S(q)$ is fulfilled. As usual the single-particle direct correlation function $C_1(q,[\rho_S])$ entering formula (3) is defined by the relation $C_1(q,[\rho_S]) = -\beta(\delta\mathcal{F}_{\mathrm{ex}}[\rho]/\delta\rho)|_{\rho=\rho_S}$. Equation (3) can be transformed into a self-consistent nonlinear integral equation for $\rho_S(q)$,

$$\rho_S(q) = Z_S^{-1}\exp\{C_1(q,[\rho_S])\}, \tag{4}$$

with the normalization constant $Z_S = \Lambda\exp(-\beta\mu) = \int\exp\{C_1(q,[\rho_S])\}dq/\langle N\rangle$.

Now we consider a bifurcation from an equilibrium reference state $\rho_{\mathrm{ref}}(q)$ [60] of symmetry $\mathcal{G}_0$ to the stationary state $\rho_S(q)$ of symmetry $\mathcal{G}_1$, where $\mathcal{G}_1$ is a subgroup of $\mathcal{G}_0$. Close to the bifurcation point the difference between the states is arbitrarily small for each q, which enables one to perform a convergent functional Taylor expansion of $\mathcal{F}_{\mathrm{ex}}[\rho]$ about $\rho_{\mathrm{ref}}(q)$. Recalling that $\mathcal{F}_{\mathrm{ex}}[\rho]$ is the generating functional of the n-particle direct correlation functions C_n [59] and introducing the dimensionless density $\overline{\rho} = \langle N\rangle v_0/V$ we find

$$\mathcal{F}_{\mathrm{ex}}[\rho_S] = \mathcal{F}_{\mathrm{ex}}[\rho_{\mathrm{ref}}] - k_BT\sum_{n=1}^{\infty}\frac{\overline{\rho}^n}{n!}\int C_n(q_1,\ldots,q_n,[P_{\mathrm{ref}}]) \times\prod_{i=1}^{n}[P_S(q_i) - P_{\mathrm{ref}}(q_i)]dq_i, \tag{5}$$

where

$$C_n(q_1,\ldots,q_n,[\rho_{\mathrm{ref}}]) = -\beta\{\delta^n\mathcal{F}_{\mathrm{ex}}[\rho]/\delta\rho(q_1)\cdots\delta\rho(q_n)\}_{\rho=\rho_{\mathrm{ref}}} = [\delta C_{n-1}/\delta\rho(q_n)]_{\rho=\rho_{\mathrm{ref}}}$$

and $\rho(q) = \overline{\rho}P(q)$. The as yet unspecified constant v_0, chosen for each system separately, has a dimension of volume and is constructed out of molecular parameters. For example, it could be taken as the molecular volume for hard-core interactions.

A straightforward consequence of the expansion (5) is that the self-consistent equation (4) reduces to a form that can directly be used in bifurcation analysis,

$$\delta P(q) = \left(\frac{Z_{\mathrm{ref}}}{Z_S}\right)P_{\mathrm{ref}}(q)\exp\left\{\sum_{n=1}^{\infty}\overline{\rho}^nK_{n+1}(q,[\delta P])\right\} - P_{\mathrm{ref}}(q) \tag{6}$$

with

$$K_{n+1}(q,[\delta P]) = \frac{1}{n!}\int C_{n+1}(q,q_1,\ldots,q_n,[P_{\mathrm{ref}}])\prod_{i=1}^{n}\delta P(q_i)dq_i \tag{7}$$

and

$$Z_S = \frac{v_0Z_{\mathrm{ref}}}{V}\int P_{\mathrm{ref}}(q)\exp\left\{\sum_{n=1}^{\infty}\overline{\rho}^nK_{n+1}(q,[\delta P])\right\} \equiv Z_{\mathrm{ref}}\overline{\exp\{\cdots\}}. \tag{8}$$

Here $\delta P(q) = P_S(q) - P_{\mathrm{ref}}(q)$, due to normalization of P_{ref} and P_S, must satisfy $\int\delta P(q)dq = 0$. Additionally, the probability $P_{\mathrm{ref}}(q)$ must be normalized to unity, which implies that $(v_0/V)\int P_{\mathrm{ref}}(q)dq = 1$ and $\overline{f(q)} = (v_0/V)\int P_{\mathrm{ref}}(q)f(q)dq$, where the latter formula is the recipe to calculate thermodynamic averages.

Clearly, by construction, Eq. (6) is satisfied by $\delta P(q) = 0$. Bifurcation analysis now seeks for nontrivial solutions that branch off from the trivial one. Assuming that the bifurcation takes place at $\overline{\rho} = \overline{\rho_0}$ we can now systematically seek for nonzero solutions to Eq. (6). In analogy to the previous works [24,61] we construct them in the vicinity of bifurcation as an expansion in an arbitrary parameter ϵ,

$$\delta P(q) = \epsilon\tau_1(q) + \epsilon^2\tau_2(q) + \cdots,$$

$$\overline{\rho} = \overline{\rho_0} + \epsilon\overline{\rho_1} + \epsilon^2\overline{\rho_2} + \cdots, \tag{9}$$

where, due to the normalization of $P(q)$ and $P_{\mathrm{ref}}(q)$, we can impose $\int\tau_n dq = 0$. By substituting Eq. (9) into Eq. (6) and comparing terms of the same order in ϵ, we easily find that equations for $\tau_n(q)$ have a hierarchical structure with respect to K_l and $\tau_m(q)$ $(m \leqslant n)$

$$\tau_1(q) = \overline{\rho_0}P_{\mathrm{ref}}(q)\{K_2(q,[\tau_1]) - \overline{K_2(q,[\tau_1])}\}, \tag{10}$$

$$\begin{aligned}\tau_2(q) = {}& \overline{\rho_0}P_{\mathrm{ref}}(q)\{K_2(q,[\tau_2]) - \overline{K_2(q,[\tau_2])}\} \\ & + \overline{\rho_1}P_{\mathrm{ref}}(q)\{K_2(q,[\tau_1]) - \overline{K_2(q,[\tau_1])}\} \\ & + \overline{\rho_0}^2P_{\mathrm{ref}}(q)\Bigg(\{\overline{K_2(q,[\tau_1])} - K_2(q,[\tau_1])\}\overline{K_2(q,[\tau_1])} \\ & + K_3(q,[\tau_1]) - \overline{K_3(q,[\tau_1])} + \frac{1}{2}\{K_2(q,[\tau_1])^2 \\ & - \overline{K_2(q,[\tau_1])^2}\}\Bigg),\end{aligned} \tag{11}$$

$$\tau_3(q) = \overline{\rho_0}P_{\mathrm{ref}}(q)\{K_2(q,[\tau_3]) - \overline{K_2(q,[\tau_3])}\} + \cdots, \tag{12}$$

$$\vdots$$

We still need equations for $\overline{\rho_n}$, the parameters that describe the direction and character of bifurcation and, hence, the order of the associated phase transition. These are found by noting that given the solution $\tau_n(q)$ the intrinsic symmetry of Eqs. (10)–(12) admits an additional class of solutions of the form $\tilde{\tau}_n(q) = \tau_n(q) + \alpha_n\tau_1(q)$, with α_n being an arbitrary parameter. Thus requiring from the start that the functions $\tau_n(q)$ are orthogonal to $\tau_1(q)$

$$\frac{v_0}{V}\int \tau_n(q)\tau_1(q)dq = \delta_{n,1}, \tag{13}$$

we fix both $\overline{\rho_{n-1}}$ and $\alpha_n=0$. Note that the existence of $\tilde{\tau}_n(q)$ expresses the freedom of monotonic reparametrization of the expansion parameter ϵ in terms of the new parameter ξ: $\epsilon=\sum_{i=1}a_i\xi^i$.

Equations (10)–(12) considerably simplify by noting that (a) the group-subgroup relation between $\mathcal{G}_0$ and $\mathcal{G}_1$ and (b) the $\mathcal{G}_0$ symmetry of $K_n(q,[P_{\text{ref}}])$ imply that $\int P_{\text{ref}}(q)\tau_1(q)dq=0$ and $\overline{K_n(q,[\tau_1])}=0$. Taking this into account we arrive at simpler equations describing the bifurcation and its character:

$$\tau_1(q) = \overline{\rho_0}P_{\text{ref}}(q)K_2(q,[\tau_1]), \tag{14}$$

$$\begin{aligned}\tau_2(q) = {} & \overline{\rho_0}P_{\text{ref}}(q)\{K_2(q,[\tau_2]) - \overline{K_2(q,[\tau_2])}\}\\ & + \overline{\rho_1}P_{\text{ref}}(q)K_2(q,[\tau_1]), + \overline{\rho_0}^2P_{\text{ref}}(q)\bigg[K_3(q,[\tau_1])\\ & + \frac{1}{2}\{K_2(q,[\tau_1])^2 - \overline{K_2(q,[\tau_1])^2}\}\bigg],\end{aligned} \tag{15}$$

$$\tau_3(q) = \overline{\rho_0}P_{\text{ref}}(q)\{K_2(q,[\tau_3]) - \overline{K_2(q,[\tau_3])}\} + \cdots, \tag{16}$$

$$\vdots$$

which are generalizations of the formulas (3.4),(3.5) from [24]. Note, particular, that $\tau_1(q)$ which bifurcates directly from $P_{\text{ref}}(q)$ is an eigenfunction of the operator that involves only the pair direct correlation function. The equations for $\tau_n(q)$, although straightforward to obtain, become quite lengthy for $n\geqslant 3$. We have constructed a MATHEMATICA package to systematically work out the expressions for $\tau_n(q)$.

Equations (13)–(16) can now directly be studied to identify the symmetry-breaking bifurcation from the equilibrium state given by $P_{\text{ref}}(q)$. They form a set of coupled integral equations for the functions τ_n, which represent actual deviations from $P_{\text{ref}}(q)$ and for $\overline{\rho_{n-1}}$.

Please note that the equations derived are exact in the vicinity of bifurcation. Consequently, the bifurcation points, which are either spinodal points for the first-order phase transitions or critical points for the continuous transitions, are fully determined from the properties of the one-particle distribution function and the direct pair correlation function of the corresponding high-symmetry equilibrium reference phase. The bifurcation points that mark the crossover from spinodal to critical type of behavior (Landau points, isolated critical points) depend additionally on the properties of the three-particle direct correlation function. Tricritical points may depend on still higher-order direct correlation functions. Perhaps we should add at this point that the direct correlation functions can be related through Ornstein-Zernike type of relations to the ordinary n-particle distribution functions [59], where the latter are easily accessible in computer simulations.

Alternatively, Eqs. (14)–(16) require an explicit formula for $\mathcal{F}_{\text{ex}}[\rho]$. There are many approximations to $\mathcal{F}_{\text{ex}}$ among which the most popular are (a) the low-density (or the generalized second-order virial) expansion,

$$\beta\mathcal{F}_{\text{ex}}[\rho] = -\frac{1}{2}\int \rho(q_1)\{\exp[-\beta W(q_1,q_2)] - 1\}\rho(q_2)dq_1dq_2 \tag{17}$$

and (b) the MF theory,

$$\beta\mathcal{F}_{\text{ex}}[\rho] = \frac{1}{2}\int \rho(q_1)[\beta W(q_1,q_2)]\rho(q_2)dq_1dq_2, \tag{18}$$

which is the high-temperature expansion of Eq. (17). In both equations the simplified notation $W(q_1,q_2)$ has been used for the pair potential.

As a first step in dealing with Eqs. (14)–(16) we need an initially stable phase. This is represented by the one-particle distribution function $P_{\text{ref}}(q)$, which, for given $\mathcal{F}_{\text{ex}}[\rho]$, can be found from an equation analogous to (4) with ρ_S being replaced by ρ_{ref}. Since the bifurcation equation (14) depends entirely on $P_{\text{ref}}(q)$ and C_2 of the reference state this generalized eigenfunction equation can be solved to find the eigenfunctions τ_1^* and the corresponding eigenvalues ρ_0^*. The eigenfunctions are related to the subgroups of $\mathcal{G}_0$ and can be expressed as linear combinations of the irreducible representations of $\mathcal{G}_0$. In general, the eigenvalues are degenerate [24] and, in order to identify the corresponding "bifurcating" phase of symmetry $\mathcal{G}_1$, one needs to refer to the higher-order equation(s) (15) that depend on higher-order direct correlation functions. The true bifurcation parameter corresponds to the minimum value of ρ_0^*, which then could be identified with $\overline{\rho_0}$.

The character of the bifurcation depends on the sign of the first nonvanishing parameter $\overline{\rho_n}$ $(n\geqslant 1)$, usually $\overline{\rho_1}$. Generally, for $\overline{\rho_1}<0$ the bifurcation is a spinodal point while for $\overline{\rho_1}>0$ it corresponds to a critical point. For $\overline{\rho_1}=0$ and $\overline{\rho_2}\neq 0$ we expect to have an isolated critical point terminating a line of first-order phase transitions. The necessary condition satisfied by the tricritical point is $\overline{\rho_1}=\overline{\rho_2}=0$. In Fig. 2 the generic bifurcation diagram is shown for critical and tricritical cases.

III. BIAXIAL ORDERING WITHIN GENERALIZED $L=2$ MODEL

The formulas of the previous section will now be studied within the MF approximation (18) [67]. Whenever possible the analysis will be carried out for a general pair potential. On the other hand, more restrictive conditions are necessary to analyze the uniaxial-to-biaxial nematic phase transition and the appearance of the tricritical point recently found by Sonnet *et al.* [12]. In this case we restrict our analysis to the generalized model of $L=2$. Special cases of this model, especially lattice ones, have already been studied by some of the authors, as explained below. We shall adopt the notation of Mulder from his paper on isotropic-symmetry-breaking bifurcation analysis for the class of hard biaxial particles

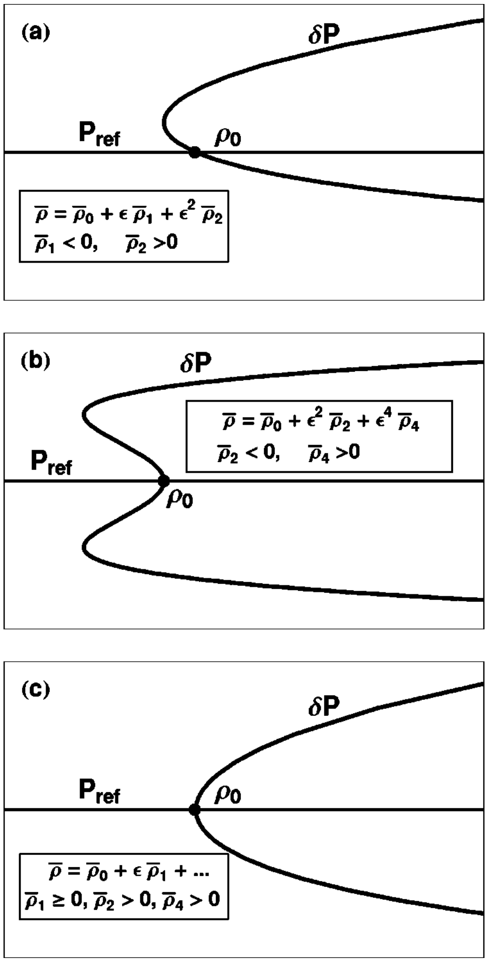

FIG. 2. Generic bifurcation diagrams (a) for a first-order phase transition, (b) for a first-order phase transition in vicinity of a tricritical point, and (c) for a continuous phase transition. The transition following the path from (b) to (c) describes a change of character of the phase transition as observed, e.g., at the tricritical point.

[24]. Notice that we do not intend to discuss relative stability of the nematic phase with respect to positionally ordered (i.e., crystalline or smectic) ones; in other words, the function $\rho(q)$ discussed in the previous section will be taken to be spatially homogeneous. The pair potential is a real scalar function $W(\mathbf{x}_1-\mathbf{x}_2,\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)$, possessing global translational and rotational invariance. It is also invariant with respect to interchange of the two particles. Consequently, W depends on the coordinates and orientations of the two interacting particles via the appropriate scalar invariants, i.e., in the formula,

$$W = W[r,(\hat{\mathbf{r}}\cdot\mathbf{b}_i),(\hat{\mathbf{r}}\cdot\boldsymbol{l}_k),(\mathbf{b}_i\cdot\boldsymbol{l}_k),\quad i,k=1,2,3]. \tag{19}$$

Moreover, the D_{2h} symmetry of particles and particle interchange symmetry entail that W is even with respect to each of the unit vectors $\hat{\mathbf{r}}$, $\mathbf{b}_i$, $\boldsymbol{l}_k$. Actually, in terms of the MF, the relevant quantity is $\widetilde{W}$, which results from W by integrating over $\mathbf{r}$; this is an even function of all terms $(\mathbf{b}_i\cdot\boldsymbol{l}_k)$. Under general conditions, $\widetilde{W}$ can be expanded in a series of S functions [62–65] or in a series of Legendre polynomials of even order.

Alternatively, $\widetilde{W}$ can be expanded in a series of symmetry-adapted functions $\Delta^{(L)}_{m,n}(\widetilde{\boldsymbol{\Omega}})$, or symmetry-adapted irreducible tensors in Cartesian form $[\widetilde{\mathbf{T}}^{(L)}_m(\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3)]_{\alpha\beta\cdots}$ and $[\widetilde{\mathbf{T}}^{(L)}_n(\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3)]_{\alpha\beta\cdots}$ in which case it reads

$$\begin{aligned}\widetilde{W} &= \sum_{L,m,n}\overline{\omega}_{L,mn}\,\Delta^{(L)}_{m,n}(\widetilde{\boldsymbol{\Omega}})\\ &= \sum_{L,m,n}\overline{\omega}_{L,mn}\,\widetilde{\mathbf{T}}^{(L)}_m(\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3)\cdot\widetilde{\mathbf{T}}^{(L)}_n(\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3),\end{aligned} \tag{20}$$

where $\Delta^{(L)}_{m,n}$ are orthogonal, D_{2h}-symmetrized linear combinations of Wigner rotation functions $\mathcal{D}^{(L)}_{m,n}(\widetilde{\boldsymbol{\Omega}})$ [66],

$$\Delta^{(L)}_{m,n} = \left(\frac{1}{2}\sqrt{2}\right)^{2+\delta_{m,0}+\delta_{n,0}}\sum_{s,t\in\{-1,1\}}\mathcal{D}^{(L)}_{sm,tn}, \tag{21}$$

$$\int d\boldsymbol{\Omega}\,\Delta^{(J)}_{m,n}(\boldsymbol{\Omega})\Delta^{(K)}_{p,q}(\boldsymbol{\Omega}) = \frac{8\pi^2}{(2J+1)}\delta_{J,K}\delta_{m,p}\delta_{n,q}. \tag{22}$$

Here $\widetilde{\boldsymbol{\Omega}}$ denotes the set of Euler angles defining the intermolecular rotation that transforms $\mathbf{b}_i$ into $\boldsymbol{l}_k$. The $[\widetilde{\boldsymbol{T}}^{(L)}_m(\mathbf{x},\mathbf{y},\mathbf{z})]$ tensors are defined as $\mathcal{G}_1$ symmetrized in Cartesian form [68]

$$\widetilde{\mathbf{T}}^{(L)}_m = c^L_m\frac{1}{|\mathcal{G}_1|}\sum_{g\in\mathcal{G}_1}\mathcal{D}(g)\mathbf{T}^{(L)}_m \tag{23}$$

where

$$\mathbf{T}^{(L)}_m = \sum_{m_1,m_2}\left(\begin{array}{cc|c} L-1 & 1 & L\\ m_1 & m_2 & m\end{array}\right)\mathbf{T}^{(L-1)}_{m_1}\otimes\mathbf{T}^{(1)}_{m_2},$$

$$\mathbf{T}^{(1)}_0 = \mathbf{z},$$

$$\mathbf{T}^{(1)}_{\pm1} = \frac{\pm1}{\sqrt{2}}(\mathbf{x}\pm i\mathbf{y}). \tag{24}$$

Here $\left(\begin{smallmatrix} L-1 & 1 & | & L\\ m_1 & m_2 & | & m\end{smallmatrix}\right)$ are the Clebsch-Gordan coefficients and $|\mathcal{G}_1|$ is the number of elements of the group $\mathcal{G}_1$. The appropriate choice of the c^L_m coefficients (23) allows the Cartesian tensors of the same rank to satisfy the orthogonality condition with respect to a scalar product defined as a full contraction over Cartesian indices,

$$\widetilde{\mathbf{T}}^{(L)}_m\cdot\widetilde{\mathbf{T}}^{(J)}_n = \sum_{\alpha,\ldots,\beta}[\widetilde{\mathbf{T}}^{(L)}_m]_{\alpha,\ldots,\beta}[\widetilde{\mathbf{T}}^{(J)}_n]_{\alpha,\ldots,\beta} = \delta_{LJ}\delta_{mn}. \tag{25}$$

The summation in the expansion (20) runs only over relevant indices given by L,m,n even, with $0\leqslant m,n\leqslant L$. Notice that particle interchange symmetry implies additionally that $\overline{\omega}_{L,mn}=\overline{\omega}_{L,nm}$, which is evident from the expansion in terms of $\widetilde{\mathbf{T}}^{(L)}_m$. In the present case, the expansion will be truncated at $L=2$, in keeping with many potential models studied in the literature and referenced in the Introduction.

It should also be noted that the formalism of $\Delta^{(L)}_{m,n}$ functions, the formalism of the irreducible Cartesian tensors $\widetilde{\mathbf{T}}^{(L)}_m$,

TABLE I. Typical models of $L=2$ studied so far in the literature.

Model	$\overline{\omega}_{2,00}$	$\overline{\omega}_{2,02}$	$\overline{\omega}_{2,22}$
Straley [5]	β	$(2/\sqrt{3})\gamma$	δ
Dispersion [16–20]	-1	$\pm\sqrt{2}\lambda$	$-2\lambda^2$
Two-tensor [12]	-1	$-\sqrt{3}\gamma$	-3λ
Amphiphilic [21]	0	0	-1

and the use of scalar products $\mathbf{b}_i \cdot \boldsymbol{l}_k$ are all completely equivalent, and each of them has some advantage depending on the specific calculations to be carried out. For convenience, the conversion formulas between the three sets of functions for the $L=2$ representation of the D_{2h} symmetry are given in the Appendix. The other geometric identities involving the scalar products that are helpful in finding relations between various models are easily obtained from them.

A. Models studied so far

The continuous interaction potentials proposed and studied in this context (see, e.g., Refs. [5,6,12,24]) can be cast in the form

$$\widetilde{W} = \epsilon[\overline{\omega}_{2,00}\Delta^{(2)}_{0,0} + \overline{\omega}_{2,02}(\Delta^{(2)}_{0,2} + \Delta^{(2)}_{2,0}) + \overline{\omega}_{2,22}\Delta^{(2)}_{2,2}]. \quad (26)$$

The maximum absolute value of the three parameters $\overline{\omega}_{2,00}$, $\overline{\omega}_{2,02}$, and $\overline{\omega}_{2,22}$, denoted ϵ, will be used to set temperature and energy scales (i.e., $T^{*}=k_B T/\epsilon$). This allows us to restrict the three scaled parameters (for which we still use the same symbol) to the interval $[-1,1]$. In many cases studied, $\overline{\omega}_{2,00}=-1$ and $\overline{\omega}_{2,22}<0$. Simulation results suggest that the condition $\overline{\omega}_{2,02}\neq 0$, $\overline{\omega}_{2,22}=0$ entails the absence of biaxial order [16] (see also below). In this sense, the choice $\overline{\omega}_{2,02}=0$, $\overline{\omega}_{2,22}<0$ defines a minimum coupling model still capable of producing biaxial ordering.

Various specific parametrizations have been proposed and studied for Eq. (26). One of them is based on an approximate mapping from a hard-block model [5]. In this case (dropping an additive constant) the $\overline{\omega}_{2,mn}$ parameters are given in terms of β, γ, and δ, Table I, where β, γ, and δ are defined by Eq. (9) in Ref. [5], in terms of length L, breadth B, and width W of the hard rectangular blocks. The case $L=10$, $W=1$ was studied in detail. The resulting mean field phase diagram exhibits an isolated Landau point for $B=\sqrt{10}$ [5].

Another and more often studied model [16] can be obtained by starting from a dispersion model at the London–de Boer–Heller approximation [68–70] and isotropically averaging over the intermolecular vector (see, e.g., Refs. [6,9]). The model [16] has been extensively studied by both MF (see, e.g., Refs. [6–11]), and Monte Carlo (MC) simulations [16–20]. According to these treatments, the maximum biaxiality can be realized by the condition $\lambda=1/\sqrt{6}$, where a direct second-order transition occurs between biaxial and isotropic phases. MF and MC estimates for this transition temperature to be found in the literature are $T_{\mathrm{MF}}=1.6$ and $T_{\mathrm{MC}}=1.09\pm 0.03$, respectively (see, e.g., Ref. [19]).

The first simulation study of the dispersion model was carried out in Ref. [16], based on the parameter values $\overline{\omega}_{2,02}=\lambda=0.2$ and $\overline{\omega}_{2,22}=-0.08$, respectively, and the model was found to produce biaxial order; on the other hand, it had also been found [16] that a truncated model defined by the same values of $\overline{\omega}_{2,00}$ and $\overline{\omega}_{2,02}$, but $\overline{\omega}_{2,22}=0$, did not support biaxial order.

The authors of Ref. [12] have examined the two-tensor model (see Table I) and, for general values of γ and λ, worked out the mathematical conditions under which the model produces a biaxial ground state, as well as its stability. They have also proposed the simplified model, defined by $\gamma=0$, and studied it by the MF method. In contrast to the two above cases showing isolated Landau points, in the resulting phase diagram (Ref. [12], Fig. 4) the biaxial-to-uniaxial transition is found to be second order for $0<\lambda\leqslant 0.20$, then first order for $0.20<\lambda\leqslant 0.22$, and finally a direct first-order transition between biaxial and isotropic phases occurs for $\lambda\geqslant 0.22$. In Ref. [12], the parameter λ was restricted to the range $0\leqslant\lambda\leqslant\frac{1}{3}$. The case $\lambda>\frac{1}{3}$ was subsequently investigated and preliminary results [71] suggest the existence of a direct biaxial-to-isotropic transition, of first or second order.

Another investigated model [21] is defined by the extreme case $\overline{\omega}_{2,00}=\overline{\omega}_{2,02}=0$, $\overline{\omega}_{2,22}=-1$, which, so to speak, pushes the simplification proposed in Ref. [12] even further; both MF and simulation results indicate here a direct biaxial-to-isotropic transition of second order; the named model can be regarded as a crude approximation to experimentally known shape-amphiphilic mesogens [21].

B. General $L=2$ model and its properties

Now we will study in detail the potential $\widetilde{W}$ resulting when the expansion is truncated at the lowest-order terms $L=2$. With a slightly simplified notation and with the help of formulas in the Appendix, it can be written down in the following equivalent forms:

$$\widetilde{W} = -|v_{00}|\{\mathrm{sgn}(v_{00})\Delta^{(2)}_{0,0}(\widetilde{\mathbf{\Omega}}) + v_0[\Delta^{(2)}_{2,0}(\widetilde{\mathbf{\Omega}}) + \Delta^{(2)}_{0,2}(\widetilde{\mathbf{\Omega}})] + v_2\Delta^{(2)}_{2,2}(\widetilde{\mathbf{\Omega}})\} \quad (27)$$

$$= -|v_{00}|\{\mathrm{sgn}(v_{00})\mathbf{L}_0\cdot\mathbf{B}_0 + v_0[\mathbf{L}_2\cdot\mathbf{B}_0 + \mathbf{L}_0\cdot\mathbf{B}_2] + v_2\mathbf{L}_2\cdot\mathbf{B}_2\} \quad (28)$$

$$= -|v_{00}|\left[(v_2-\sqrt{3}v_0)(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2 + (v_2+\sqrt{3}v_0)(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2 + \left(\frac{3}{2}\mathrm{sgn}(v_{00}) - \frac{v_2}{2}\right)(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2 - \frac{\mathrm{sgn}(v_{00})+v_2}{2}\right] \quad (29)$$

$$= -\widetilde{v}_1(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2 - \widetilde{v}_2(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2 - \widetilde{v}_3(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2 + \mathrm{const}, \quad (30)$$

where the Cartesian counterparts $\mathbf{L}_m=\widetilde{\mathbf{T}}^{(2)}_m(\{\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3\})$ and $\mathbf{B}_m=\widetilde{\mathbf{T}}^{(2)}_m(\{\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3\})$ of Δ functions are given in the Appendix. As already indicated above and in [12], formulas (28) and (29) for the potential in terms of orthonormal triplets of vectors, Fig. 1, and their scalar products, are more appealing than the one with symmetrized $\Delta^{(L)}_{m,n}$ functions (see the Appendix for details), since they clearly display the symmetry of the interaction and the meaning of the coupling constants. On the other hand, in practical calculations of the mean field type, the representation in terms of symmetry-adapted functions allows one to use the orthogonality properties (22), resulting in an enormous simplification.

Symmetry of the expression (29), which is a complete equivalence of the axes of the tripods associated with the molecules, implies that the thermodynamics cannot change if we permute $\tilde{v}_i$ among different $(\mathbf{b}_k\cdot\boldsymbol{l}_k)^2$ terms. Consequently the sign of v_0 in Eq. (29) is irrelevant and we could either replace v_0 by $|v_0|$ or consider only positive values of v_0. In carrying out numerical analysis we shall restrict ourselves to $v_0\geqslant 0$. Moreover at least one of $\tilde{v}_i$ must be positive. If all the coupling constants are negative we do not get a stable nematic phase. Again, doing numerical calculations we assume that $\tilde{v}_3>0$.

A further symmetry of the potential (27) is found if the permutation symmetry of (29) is combined with the requirement that $\beta\tilde{W}$ is left invariant during such operation. This yields a nontrivial *duality transformation* between states at various temperatures. More specifically, suppose that we simultaneously change the "2" and "3" axes of the molecules and substitute $\{\mathrm{sgn}(v_{00}),|v_{00}|v_0,v_2\}$ with $\{\mathrm{sgn}(v'_{00}),|v'_{00}|,v'_0,v'_2\}$, where

$$\mathrm{sgn}(v'_{00})|v'_{00}| = \frac{1}{4}[\mathrm{sgn}(v_{00}) + 2\sqrt{3}v_0 + 3v_2]|v_{00}|, \tag{31}$$

$$\mathrm{sgn}(v'_{00})v'_0 = \frac{6v_0^2 + \sqrt{3}v_0[3\,\mathrm{sgn}(v_{00}) - v_2] + 3[\mathrm{sgn}(v_{00}) - v_2]v_2}{[\mathrm{sgn}(v_{00}) + 2\sqrt{3}v_0 + 3v_2](3v_0 + \sqrt{3}v_2)}, \tag{32}$$

$$\mathrm{sgn}(v'_{00})v'_2 = \frac{-6v_0 + \sqrt{3}[3\,\mathrm{sgn}(v_{00}) + v_2]}{6v_0 + \sqrt{3}[\mathrm{sgn}(v_{00}) + 3v_2]}. \tag{33}$$

By simple inspection we find that this so called duality transformation, referred to as $\mathcal{D}_{23}$, leaves $\beta\tilde{W}$ invariant, which implies that the thermodynamic results for particles interacting through parameters $\{v_0,v_2\}$ and temperature $t=k_BT/|v_{00}|$ are the same as for those interacting through $\{v'_0,v'_2\}$ at $t'=k_BT/|v'_{00}|$. The self-dual case, defined by the equations $v'_0=v_0$, $v'_2=v_2$, obeys all points lying on the line $v_2=\mathrm{sgn}(v_{00})-2v_0/\sqrt{3}$ and the point $\{v_0,v_2\}=\{-\mathrm{sgn}(v_{00})/\sqrt{3},-\mathrm{sgn}(v_{00})\}$ $(v_{00}=0)$. The line $v_2=\mathrm{sgn}(v_{00})-2v_0/\sqrt{3}$ for $v_0\geqslant 0$ and for $\mathrm{sgn}(v_{00})=1$ separates states of predominantly prolate symmetry from those of predominantly oblate one.

The duality transformation $\mathcal{D}_{13}$, involving axes "1" and "3" yields equations similar to Eqs. (31)–(33), but with (v_0,v'_0) being replaced by $(-v_0,-v'_0)$. The third possible duality transformation $\mathcal{D}_{12}$ gives $v'_0=-v_0$, $v'_2=v_2$, and $v'_{00}=v_{00}$, which is in line with the observation that the equilibrium states of v_0 and $-v_0$ are identical, in agreement with the aforementioned permutation symmetry of Eq. (29).

It is instructive to study the action of $\mathcal{D}_{23}$ on the parameter space $\{v_0,v_2\}$. For $\mathrm{sgn}(v_{00})=1$ this is shown in Fig. 2, where five distinct areas, denoted $A,\ldots,E$ are identified together with their $\mathcal{D}_{23}$ images $A_{23},\ldots,E_{23}$. These areas are separated by self-dual (continuous and straight) lines $v_2=1-2v_0/\sqrt{3}$, $v_2=1+2v_0/\sqrt{3}$, and $v_0=0$ of $\mathcal{D}_{23}$, $\mathcal{D}_{13}$, and $\mathcal{D}_{12}$, respectively, and by the dashed straight lines $v_2=-1/3-2v_0/\sqrt{3}$, $v_2=-1/3+2v_0/\sqrt{3}$, where v'_{00} of $\mathcal{D}_{23}$ and $\mathcal{D}_{13}$ vanishes. The three self-dual lines cross at the point $\{v_0,v_2\}=\{0,1\}$ of maximal symmetry, where all coupling constants of the model (29) are equal. Along self-dual lines two out of the three coupling constants become degenerate. Finally, the dot in Fig. 2 represents the isolated, $\mathcal{D}_{23}$ self-dual point at $\{v_0,v_2\}=\{-1/\sqrt{3},-1\}$.

It is sufficient to generate phase diagrams for the parameters taken from the shaded area A in Fig. 2. The diagrams for the remaining values of the parameters are obtained by systematic application of the duality transformations. The parameters from A correspond to states of predominantly prolate symmetry while the image states A_{23} are of predominantly oblate symmetry. Therefore the self-dual line of $\mathcal{D}_{23}$ is expected to separate states of oblate symmetry from those of prolate symmetry.

The interaction as given includes only the expansion terms involving $L=2$. It is the simplest possible case; however, it is sufficient for the study of biaxial and uniaxial nematic phases. The $L=2$ model could be considered as a generalization of the well-known Maier-Saupe or Lebwohl-Lasher interactions. The only difference is that instead of one vector attached to a molecule we are dealing with three orthonormal vectors as our molecules require three axes to characterize their orientation in space. Some special cases of the $L=2$ interaction have already been studied in the literature and summarized in the previous subsection. Some relevant for further analysis are collected in Table I. In particular, the gray curve in Fig. 3 corresponds to the (ϵ,λ) model studied by Biscarini *et al.* [18], for which $v_0=\sqrt{2}\lambda\geqslant 0$, $v_2=2\lambda^2$, and $v_{00}=\epsilon>0$. It crosses the self-dual line at $\{v_0,v_2\}=\{1/\sqrt{3},1/3\}$, which is exactly the self-dual point predicted in [18].

C. Bifurcation analysis

Now we apply formulas (14)–(16) to study bifurcation from the isotropic and the uniaxial nematic phases to the biaxial nematic phase. As an example we will work out in detail the MF formulas for $\mathcal{F}_{\mathrm{ex}}$, Eq. (18), which amount to solving the MF version

$$\rho(q) = Z^{-1}\exp\left[-\beta\int W(q,\bar{q})\rho(\bar{q})d\bar{q}\right] \tag{34}$$

of the self-consistent equation (4) for $\rho(q)$, with $\rho(q)\equiv\rho_S(q)$ or $\rho(q)\equiv\rho_{\mathrm{ref}}$, and, subsequently, Eqs. (14)–(16).

Disregarding spatially ordered phases, like smectic and crystalline ones, and assuming that $v_0P(q)\equiv P(\mathbf{\Omega})$, $v_0\tau_n(q)\equiv\tau_n(\mathbf{\Omega})$ and $(1/V)\int d\mathbf{q}\equiv\int d\mathbf{\Omega}$ $[\int d\mathbf{\Omega}\,P(\mathbf{\Omega})=1]$ possesses the same symmetry as our pair interaction $\bar{v}$ we can expand the distribution function $P(\mathbf{\Omega})$ in the Δ functions,

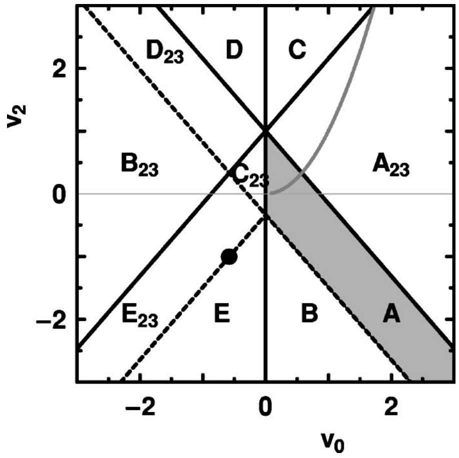

FIG. 3. Action of the nontrivial duality transformation $\mathcal{D}_{23}$ on the parameter space $\{v_0, v_2\}$ for $\mathrm{sgn}(v_{00})=1$. Self-dual points are the line $v_2=\mathrm{sgn}(v_{00})-2v_0/\sqrt{3}$ and the isolated point $\{v_0, v_2\}=\{-\mathrm{sgn}(v_{00})/\sqrt{3}, \mathrm{sgn}(v_{00})\}(v_{00}=0)$ indicated by dot. Five different areas $A,\ldots,E$ and the corresponding $\mathcal{D}_{23}$ images $A_{23},\ldots,E_{23}$ are distinguished. The gray line corresponds to the parameter set studied by Biscarini *et al.* [18]. The points belonging to lines $v_2=-1/3-2|v_0|/\sqrt{3}$ are not self-dual except for the point above, but the line itself is left invariant under $\mathcal{D}_{23}$. Self-dual points $\{v_0=0, v_2 \geqslant 1\}$ correspond to the biaxial phase.

$$P(\mathbf{\Omega}) = \sum_{L,m,n} \frac{2L+1}{8\pi^2}\overline{\Delta_{m,n}^{(L)}}\Delta_{m,n}^{(L)}(\mathbf{\Omega}), \tag{35}$$

where

$$\overline{\Delta_{m,n}^{(L)}} = \int d\mathbf{\Omega}\; P(\mathbf{\Omega})\Delta_{m,n}^{(L)}(\mathbf{\Omega}) \tag{36}$$

are the order parameters for $L \geqslant 2$. Using this expansion, the self-consistent equation (34) now becomes

$$\begin{aligned} P(\mathbf{\Omega}) = Z^{-1}\exp\Bigg(\frac{1}{t}\{&[\mathrm{sgn}(v_{00})\overline{\Delta_{0,0}^{(2)}} + v_0\overline{\Delta_{0,2}^{(2)}}]\Delta_{0,0}^{(2)}(\mathbf{\Omega}) \\ &+ (v_0\overline{\Delta_{0,0}^{(2)}} + v_2\overline{\Delta_{0,2}^{(2)}})\Delta_{0,2}^{(2)}(\mathbf{\Omega}) + [\mathrm{sgn}(v_{00})\overline{\Delta_{2,0}^{(2)}} \\ &+ v_0\overline{\Delta_{2,2}^{(2)}}]\Delta_{2,0}^{(2)}(\mathbf{\Omega}) + (v_0\overline{\Delta_{2,0}^{(2)}} + v_2\overline{\Delta_{2,2}^{(2)}})\Delta_{2,2}^{(2)}(\mathbf{\Omega})\}\Bigg), \end{aligned} \tag{37}$$

with $t=k_BT/|v_{00}|\overline{\rho}$ being the dimensionless temperature. For lattice models $\overline{\rho}$ should be replaced by the lattice coordination number. Equation (37) could be solved iteratively by taking regard of the definition (36); namely, by performing an expansion of the one-particle distribution function on the left-hand side of Eq. (37) in the basis of symmetry-adapted Δ_{mn}^{L} functions, multiplying both sides by $\Delta_{m'n'}^{L'}$, and integrating over Euler angles, which yields an equivalent set of the self-consistent equations for the order parameters $\overline{\Delta_{m,n}^{(2)}}$. An alternative, and much simpler, bifurcation analysis follows directly from Eqs. (13)–(16).

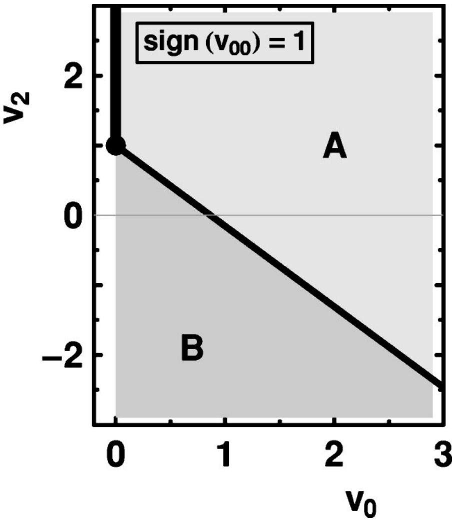

FIG. 4. Division of parameter space $\{v_0, v_2\}$ for $\mathrm{sgn}(v_{00})>0$ according to the bifurcation phase diagram from the isotropic phase. Uniaxial disklike states bifurcate for the parameters located in the area A. Area B corresponds to rodlike states and the thick line represents the biaxial nematic phase. The self-dual line is a collection of Landau points.

Three classes of solutions are identified: (a) the isotropic phase of $\overline{\Delta_{m,n}^{(L)}}=0$, being always the solution of Eq. (37); (b) the uniaxial prolate or oblate nematic phase; and (c) the biaxial phase.

The bifurcation from the isotropic phase to uniaxial phases for Eq. (37) has been studied thoroughly by Mulder [24]. In particular, the bifurcation equation (14) yields the bifurcation temperature t_*, which in our notation is given by

$$t_* = \frac{1}{10}[\mathrm{sgn}(v_{00}) + v_2 + \sqrt{(\mathrm{sgn}(v_{00}) - v_2)^2 + 4v_0^2}]. \tag{38}$$

Equation (38) is exact within the MF approximation for the potential (27). Actually, it is exact for a much more general class of pair interactions as discussed in [24]. According to Eq. (10), the same formula is also obtained by replacing the potential parameters $\overline{v}_{L,mn}$ with the corresponding structural parameters $\overline{C}_{2,L,mn}$ of the direct pair correlation function C_2. In this latter case, however, Eq. (38) becomes more complicated as the coefficients-$\overline{C}_{2,L,mn}$ themselves depend on the temperature. Hence, in this case Eq. (38) becomes a self-consistent equation for t_*.

The parameters of crossover between prolate and oblate uniaxial order (Landau points) are given by equating to zero Eq. (3.19) of [24]. It yields $v_2=1-2|v_0|/\sqrt{3}$, which matches the self-dual lines of $\mathcal{D}_{13}$ and $\mathcal{D}_{23}$ for $v_2 \leqslant 1$, indicating that the mean field approximation is consistent with the duality properties of the model. A full bifurcation scenario from the isotropic phase to biaxial and uniaxial phases is illustrated in Figs. 4 and 5.

With the help of Eqs. (14)–(16) and (34)–(37) we are able to derive exact formulas for the bifurcation temperature t_* between uniaxial and biaxial nematic phases. It reads

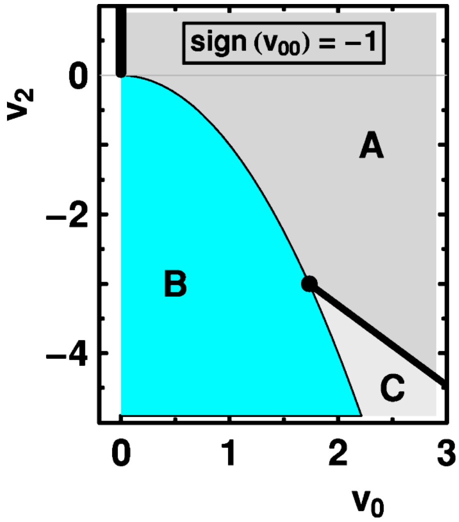

FIG. 5. Division of parameter space $\{v_0, v_2\}$ for $\mathrm{sgn}(v_{00})<0$ according to the bifurcation phase diagram from the isotropic phase. Uniaxial disklike states bifurcate for the parameters located in the area *A*. In the area *B*, separated from *A* and *C* by the parabola $v_2 = -v_0^2$, no stable nematic phase exists. Area *C* corresponds to rodlike states and the thick line represents the biaxial nematic phase. The self-dual line is a collection of Landau points.

$$v_2 = \frac{(a^2 - bc)v_0^2 - [\mathrm{sgn}(v_{00})c + 2av_0]t_* + t_*^2}{\mathrm{sgn}(v_{00})(a^2 - bc) + bt_*}, \tag{39}$$

where

$$70a = 20\overline{\Delta^{(2)}_{0,2}} + \sqrt{15}\,\overline{\Delta^{(4)}_{0,2}}, \tag{40}$$

$$70b = 14 + 20\overline{\Delta^{(2)}_{0,0}} + \overline{\Delta^{(4)}_{0,0}} + \sqrt{35}\,\overline{\Delta^{(4)}_{0,4}}, \tag{41}$$

$$70c = 14 - 20\overline{\Delta^{(2)}_{0,0}} + 6\overline{\Delta^{(4)}_{0,0}}. \tag{42}$$

The additional condition that the bifurcation point is the tricritical one reads

$$\begin{aligned}
&3\overline{\eta_2^2}^2 - \overline{\eta_2^4} + 3t_*^2\{[\overline{\xi_0^2} - \overline{\xi_0}^2 - t_*\mathrm{sgn}(v_{00})]e^2 - 2(\overline{\eta_0\xi_0} - \overline{\eta_0\xi_0}\\
&\quad + t_*v_0)ef - (\overline{\eta_0}^2 - \overline{\eta_0^2} + t_*v_2)f^2\} + 6\overline{\eta_2^2}d(2\overline{\eta_2\xi_2} + d\overline{\xi_2^2})\\
&\quad + d\{-4\overline{\eta_2^3\xi_2} + d[12\overline{\eta_2\xi_2}^2 - 6\overline{\eta_2^2\xi_2^2} + 4(3\overline{\eta_2\xi_2}\,\overline{\xi_2^2} - \overline{\eta_2\xi_2^3})d\\
&\quad + (3\overline{\xi_2^2}^2 - \overline{\xi_2^4})d^2]\} = 0,
\end{aligned} \tag{43}$$

where

$$d = \frac{\overline{\eta_2\xi_2} - t_*v_0}{t_*\mathrm{sgn}(v_{00}) - \overline{\xi_2^2}}, \tag{44}$$

$$e = g[g_3(\ln Z_{2,3}t_* - v_0) - g_2(\ln Z_{3,3}t_* - v_2)], \tag{45}$$

$$f = g[-g_3(\ln Z_{2,2}t_* - \mathrm{sgn}(v_{00})) + g_2(\ln Z_{2,3}t_* - v_0)], \tag{46}$$

$$\begin{aligned}
g^{-1} = t_*^{-1}Z_0[(\ln Z_{2,3}t_* - v_0)^2 - (\ln Z_{2,2}t_* - \mathrm{sgn}(v_{00})\\
\times(\ln Z_{3,3}t_* - v_2)],
\end{aligned} \tag{47}$$

$$\begin{aligned}
g_m = \ln Z_m Z_{0,0} - Z_{0,0,m} + d[2\ln Z_m Z_{0,1} - 2Z_{0,1,m}\\
+ d(\ln Z_m Z_{1,1} - Z_{1,1,m})],
\end{aligned} \tag{48}$$

and where $Z \equiv Z_0$, Eq. (37), and derivatives of Z with respect to $x_0 \equiv \overline{\Delta^{(2)}_{2,2}}$, $x_1 \equiv \overline{\Delta^{(2)}_{2,0}}$, $x_2 \equiv \overline{\Delta^{(2)}_{0,0}}$, $x_3 \equiv \overline{\Delta^{(2)}_{0,2}}$ are taken in the uniaxial nematic phase, stable at t_*. Also the order parameters $\overline{\Delta^{(L)}_{0,n}}$ and the averages involving $\xi_m = \mathrm{sgn}(v_{00})\Delta^{(2)}_{m,0} + v_0\Delta^{(2)}_{m,2}$, $\eta_m = v_0\Delta^{(2)}_{m,0} + v_2\Delta^{(2)}_{m,2}$ must be determined in the uniaxial nematic phase. Similar formulas can be derived by projecting out the theory (2) onto Landau expansion about the isotropic and the uniaxial nematic phases [72–74].

Numerical analysis of the bifurcation equations is presented in Figs. 6 and 7. More specifically, Figs. 6 and 7 show an approximate phase diagram collecting bifurcation points, parametrized by temperature and potential parameters. Sketched is the reduced temperature as a function of the interaction parameters v_0, v_2. Crosses indicate localization of the tricritical points. Note that below the tricritical point temperature, where the phase transitions are second order, the bifurcation points match with the true MF phase diagram. In all other cases they limit the true phase diagram from

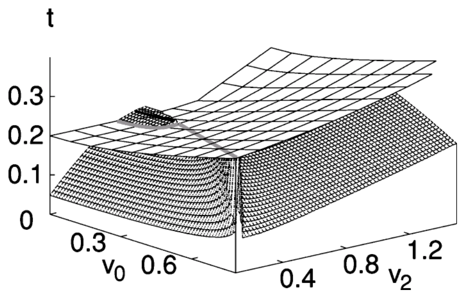

FIG. 6. Complete bifurcation diagram for $\mathrm{sgn}(v_{00})>0$. The upper surface, tailed by larger squares, represents bifurcation from the isotropic phase. The second surface gives the bifurcation temperature from uniaxial to biaxial states. Tricritical temperatures are marked with continuous, black line.

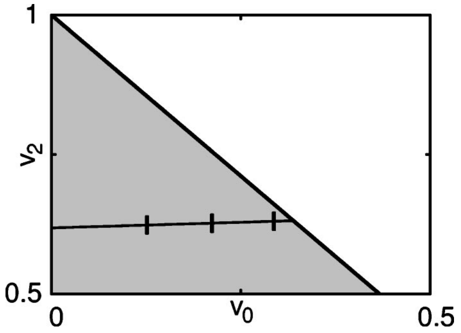

FIG. 7. v_2 versus v_0 at tricritical point. Only tricritical points in the area *A* of Fig. 3 are shown. The remaining can be obtained by a systematic application of duality transformations. Tricritical temperature varies from $t_*=0.2147$ for $v_0=0$ to $t_*=0.2367$ at $v_0=0.3194$, where the tricritical line meets the self-dual line $v_2=1-(2/\sqrt{3})v_0$. Tick marks correspond to intermediate, equally spaced temperatures.

below. The diagrams are representative for prolatelike molecules, localized in the area A of Fig. 3. We draw the areas of (a) the direct isotropic-biaxial phase transition, (b) the isotropic-uniaxial-biaxial phase transition, and the area where no stable nematic phase is obtained. Having nematic phases and tricritical points localized in the area A of Fig. 3 we can now recover all other phase diagrams and (tri)critical points of the model by systematic application of the duality transformations. Our results agree with those found earlier for $\upsilon_0=0$ [12]. Note a weak dependence of the tricritical temperature on υ_0 and the possibility of having a tricritical Landau point where the self-dual line crosses the tricritical one.

IV. SUMMARY

Recent experiments [52–54] seem to provide firm evidence for the existence of a stable thermotropic biaxial nematic phase. Search for this phase has been ongoing for more than 30 years now and one of the questions addressed was as to why the phase is so elusive. In order to provide at least partial understanding of this issue we generalized the existing bifurcation theories [24,72,74] to find thermodynamically exact criteria that govern the stability of the phase. We showed explicitly that the bifurcation to the biaxial nematic phase is given by the direct pair correlation function of the underlying high-symmetry phase (isotropic or uniaxial nematic) and we proved the hierarchical role played by the higher-order direct correlation functions in determining the order of the transition. The derived formulas indicate the importance of the $L=2$ model in a proper understanding of biaxial ordering. Though the model was introduced in the literature some time ago [6,16] only partial information about its thermodynamic properties was available (see Sec. III A and Table I for a summary). We carried out the complementary analysis. In particular we concentrated on the duality properties of the model, which provide a link between predominantly prolate and predominantly oblate states, dividing the parameter space into corresponding sectors.

In Sec. III we derived the mean field bifurcation temperature between the uniaxial and biaxial nematic phases within the model and formulas identifying the character of this bifurcation. They tell us whether the transition is first order or continuous. In principle, a more general analysis that is thermodynamically exact up to the angular momentum index $L=2$ could easily be carried out if instead of expanding the pair potential in symmetry-adapted basis functions we expanded the structural quantities C_2 and C_3. The formulas derived remain valid provided that we disregard C_n, $n\geqslant 3$, disregard director dependence in C_2, and limit to $L=2$ terms in the expansion of C_2.

The classification of the potential parameters as given in Figs. 3–7 could be used in rough guesses as to whether any other model aiming at reproducing the biaxial nematic phase could really have a chance to do it. Indeed, by a simple projection of any potential into the $L=2$ subspace we could immediately identify which part of the interaction parameter space of Fig. 3 the model is likely to occupy. This analysis could be useful in seeking for the optimal model producing the biaxial nematic phase and thus may help in identifying directions to follow to get a stable thermotropic biaxial phase in realistic materials. Clearly, the most promising direction to follow is to get materials (molecular models) with interactions localized in the vicinity of self-dual lines, especially the ones with $\upsilon_0\approx 0$ and $\upsilon_2\gtrsim 1$.

A nontrivial question that should still be addressed is whether the MF-predicted tricritical behavior can be accounted for when fluctuations of orientational order are taken into account.

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APPENDIX: SYMMETRY ADAPTED $\Delta^{(2)}_{m,n}$ FUNCTIONS AND $\tilde{\mathbf{T}}^{(2)}_{m}$ TENSORS VS DIRECTIONAL COSINES

Here we list all relevant Δ functions and irreducible $\tilde{\mathbf{T}}$ tensors used in the paper and their relation to directional cosines. For $L=2$ there are only four D_{2h}-symmetric, independent Δ's and two $\tilde{\mathbf{T}}$ tensors for each orthonormal tripod of vectors. Consequently, only four squares of directional cosines out of nine $(\mathbf{b}_\alpha\cdot\boldsymbol{l}_\beta)^2$ could be chosen independently. Decomposition of $(\mathbf{b}_\alpha\cdot\boldsymbol{l}_\beta)^2$ in the basis of $\Delta^{(2)}_{m,n}$ reads

$$(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2=\frac{1}{6}[2+\Delta^{(2)}_{0,0}+3\Delta^{(2)}_{2,2}-\sqrt{3}(\Delta^{(2)}_{0,2}+\Delta^{(2)}_{2,0})], \quad \text{(A1)}$$

$$(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2=\frac{1}{6}[2+\Delta^{(2)}_{0,0}+3\Delta^{(2)}_{2,2}+\sqrt{3}(\Delta^{(2)}_{0,2}+\Delta^{(2)}_{2,0})], \quad \text{(A2)}$$

$$(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2=\frac{1}{3}(1+2\Delta^{(2)}_{0,0}), \quad \text{(A3)}$$

$$(\mathbf{b}_1\cdot\boldsymbol{l}_2)^2=\frac{1}{6}[2+\Delta^{(2)}_{0,0}-3\Delta^{(2)}_{2,2}-\sqrt{3}(\Delta^{(2)}_{0,2}-\Delta^{(2)}_{2,0})] \quad \text{(A4)}$$

$$(\mathbf{b}_2\cdot\boldsymbol{l}_1)^2=\frac{1}{6}[2+\Delta^{(2)}_{0,0}-3\Delta^{(2)}_{2,2}+\sqrt{3}(\Delta^{(2)}_{0,2}-\Delta^{(2)}_{2,0})] \quad \text{(A5)}$$

$$(\mathbf{b}_1\cdot\boldsymbol{l}_2)^2+(\mathbf{b}_2\cdot\boldsymbol{l}_1)^2=1-(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2-(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2+(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2 \quad \text{(A6)}$$

$$(\mathbf{b}_1\cdot\boldsymbol{l}_3)^2=\frac{1}{3}(1-\Delta^{(2)}_{0,0}+\sqrt{3}\Delta^{(2)}_{0,2}) \quad \text{(A7)}$$

$$(\mathbf{b}_3\cdot\boldsymbol{l}_1)^2=\frac{1}{3}(1-\Delta^{(2)}_{0,0}+\sqrt{3}\Delta^{(2)}_{2,0}) \quad \text{(A8)}$$

$$(\mathbf{b}_1\cdot\boldsymbol{l}_3)^2+(\mathbf{b}_3\cdot\boldsymbol{l}_1)^2=1-(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2+(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2-(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2 \tag{A9}$$

$$(\mathbf{b}_2\cdot\boldsymbol{l}_3)^2=\frac{1}{3}(1-\Delta^{(2)}_{0,0}-\sqrt{3}\Delta^{(2)}_{0,0}) \tag{A10}$$

$$(\mathbf{b}_3\cdot\boldsymbol{l}_2)^2=\frac{1}{3}(1-\Delta^{(2)}_{0,0}-\sqrt{3}\Delta^{(2)}_{2,0}) \tag{A11}$$

$$(\mathbf{b}_2\cdot\boldsymbol{l}_3)^2+(\mathbf{b}_3\cdot\boldsymbol{l}_2)^2=1+(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2-(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2-(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2, \tag{A12}$$

where the relative Euler angles $\tilde{\boldsymbol{\Omega}}$ in the argument of $\Delta^{(2)}_{m,n}$ have been left out for clarity.

Construction of relevant $\mathbf{T}^{(L)}$ tensors and of their symmetrized counterparts follows easily from Eq. (24). In particular, for an arbitrary right-handed orthonormal tripod $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ the $\mathbf{T}^{(0)}(\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\})\equiv\mathbf{T}^{(0)}$ and $\mathbf{T}^{(2)}(\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\})\equiv\mathbf{T}^{(2)}$ tensors are

$$\mathbf{T}^{(0)}_0=\frac{1}{\sqrt{3}}\mathbf{1} \tag{A13}$$

$$\mathbf{T}^{(2)}_{\pm 2}=\frac{1}{2}(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}})\otimes(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}}) \tag{A14}$$

$$\mathbf{T}^{(2)}_{\pm 1}=\mp\frac{1}{2}[(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}})\otimes\hat{\mathbf{z}}+\hat{\mathbf{z}}\otimes(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}})] \tag{A15}$$

$$\mathbf{T}^{(2)}_0=\frac{1}{\sqrt{6}}[3\hat{\mathbf{z}}\otimes\hat{\mathbf{z}}-\mathbf{1}] \tag{A16}$$

$$\mathbf{1}=\hat{\mathbf{x}}\otimes\hat{\mathbf{x}}+\hat{\mathbf{y}}\otimes\hat{\mathbf{y}}+\hat{\mathbf{z}}\otimes\hat{\mathbf{z}}. \tag{A17}$$

The D_{2h} symmetrization yields $\tilde{\mathbf{T}}^{(0)}_0=\mathbf{T}^{(0)}_0$ and leaves only two nonvanishing, independent tensors $\tilde{\mathbf{T}}^{(2)}_m$,

$$\tilde{\mathbf{T}}^{(2)}_0=\mathbf{T}^{(2)}_0, \tag{A18}$$

$$\tilde{\mathbf{T}}^{(2)}_2=\frac{1}{\sqrt{2}}(\hat{\mathbf{x}}\otimes\hat{\mathbf{x}}-\hat{\mathbf{y}}\otimes\hat{\mathbf{y}}), \tag{A19}$$

which correspond to the tensors q and b used in [12]. Note that up to $L=2$ there are only three irreducible tensors built out of an orthonormal tripod that are consistent with D_{2h} symmetry: isotropic $\mathbf{T}^{(0)}_0$, uniaxial $\mathbf{T}^{(2)}_0$, and biaxial $\mathbf{T}^{(2)}_2$ of maximal biaxiality ($\mathrm{Tr}[(\mathbf{T}^{(2)}_2)^3]=0$). Further applications of the Cartesian irreducible tensors to study chiral and biaxial systems are found in [75–77].

All possible relations between dependent $(\mathbf{b}_\alpha\cdot\boldsymbol{l}_\beta)^2$ could now easily be derived. In particular, from Eqs. (A1)–(A19) one finds one possible set of relations:

$$\Delta^{(2)}_{0,0}(\tilde{\boldsymbol{\Omega}})=\mathbf{L}_0\cdot\mathbf{B}_0=\frac{1}{4}+\frac{3\cos(2\,\tilde{\beta})}{4}=-\frac{1}{2}+\frac{3}{2}(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2, \tag{A20}$$

$$\begin{aligned}\Delta^{(2)}_{0,2}(\tilde{\boldsymbol{\Omega}})=\mathbf{L}_0\cdot\mathbf{B}_2&=\frac{\sqrt{3}}{2}\cos(2\,\tilde{\gamma})\sin(\tilde{\beta})^2\\&=\frac{\sqrt{3}}{2}[(\mathbf{b}_1\cdot\boldsymbol{l}_3)^2-(\mathbf{b}_2\cdot\boldsymbol{l}_3)^2],\end{aligned} \tag{A21}$$

$$\begin{aligned}\Delta^{(2)}_{2,0}(\tilde{\boldsymbol{\Omega}})=\mathbf{L}_2\cdot\mathbf{B}_0&=\frac{\sqrt{3}}{2}\cos(2\tilde{\alpha})\sin(\tilde{\beta})^2\\&=\frac{\sqrt{3}}{2}[(\mathbf{b}_3\cdot\boldsymbol{l}_1)^2-(\mathbf{b}_3\cdot\boldsymbol{l}_2)^2],\end{aligned} \tag{A22}$$

$$\begin{aligned}\Delta^{(2)}_{2,2}(\tilde{\boldsymbol{\Omega}})&=\mathbf{L}_2\cdot\mathbf{B}_2\\&=\frac{1}{4}\cos(2\tilde{\alpha})[3+\cos(2\tilde{\beta})]\cos(2\tilde{\gamma})\\&\quad-\cos(\tilde{\beta})\sin(2\tilde{\alpha})\sin(2\tilde{\gamma})\\&=(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2+(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2-\frac{1}{2}(\mathbf{b}_3\cdot\boldsymbol{l}_3)^2-\frac{1}{2},\end{aligned} \tag{A23}$$

$$\Delta^{(2)}_{2,0}(\tilde{\boldsymbol{\Omega}})+\Delta^{(2)}_{0,2}(\tilde{\boldsymbol{\Omega}})=\sqrt{3}[(\mathbf{b}_2\cdot\boldsymbol{l}_2)^2-(\mathbf{b}_1\cdot\boldsymbol{l}_1)^2], \tag{A24}$$

where $\mathbf{L}_m=\tilde{\mathbf{T}}^{(2)}_m(\{\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3\})$ and $\mathbf{B}_m=\tilde{\mathbf{T}}^{(2)}_m(\{\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3\})$.

Considering the orthonormal tripod $\{\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3\}$ as being associated with symmetry axes of the nematic phase and fixing $\{\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3\}$ to a molecule, Eqs. (A10)–(A14) allow one to construct linear combinations of Δ functions that satisfy symmetry restrictions imposed by various nematic phases. For example, the state $a\,\Delta^{(2)}_{0,0}+b\,\Delta^{(2)}_{0,2}$ being the linear combination of $\Delta^{(2)}_{0,0}$ and $\Delta^{(2)}_{0,2}$ describes the uniaxial phase invariant under rotation about $\boldsymbol{l}_3$.

Similarly, the states $a(\Delta^{(2)}_{0,0}+\sqrt{3}\Delta^{(2)}_{2,0})+b(\Delta^{(2)}_{0,2}+\sqrt{3}\Delta^{(2)}_{2,2})$, and $a(\Delta^{(2)}_{0,0}-\sqrt{3}\Delta^{(2)}_{2,0})+b(\Delta^{(2)}_{0,2}-\sqrt{3}\Delta^{(2)}_{2,2})$ describe the nematic phases uniaxial about $\boldsymbol{l}_2$ and $\boldsymbol{l}_1$, respectively. The above properties follow immediately from Eqs. (A2), (A11), (A5), and (A8).

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