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Dielectric shape dispersion and biaxial transitions in nematic liquid crystals

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Using two order tensors, we propose a mean-field model to describe the uniaxial and biaxial phases of nematogenic molecules presenting a shape dispersion of their biaxial dielectric susceptibility. We recover the classical isotropic-uniaxial-biaxial sequence of phases. The phase diagram exhibits a tricritical point, a feature that cannot be retraced in the other mean-field models established for molecules without shape dispersion.

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I. INTRODUCTION

Biaxial nematic liquid crystals are still fascinating objects from both experimental and theoretical points of view. Although stable biaxial phases have unmistakably been observed in lyotropic systems since the pioneering work of Yu and Saupe [1], the experimental evidence in favor of their existence in thermotropic systems is still highly disputed (see, for example, Ref. [2] for a recent overview of this long vexed question and Refs. [3,4] for a new approach to it).

Most nematogenic molecules are intrinsically biaxial. Usually, they give rise to uniaxial phases as a consequence of the rotational disorder around the long molecular axis, which eventually results in the definition of a single macroscopic director. However, this rotational disorder can be hampered by interactions favoring the molecules to stick parallel to one another: at low enough temperatures, these interactions should promote a biaxial nematic phase. In the past 30 years, the description of such biaxial phases has posed many interesting problems. At a macroscopic scale, the nematic order is traditionally described by a symmetric, traceless tensor **Q** of rank two. A general representation of **Q** is given by

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

where **I** is the identity tensor and S and T are scalar order parameters. In Eq. (1), $\{\boldsymbol{e}_x,\boldsymbol{e}_y,\boldsymbol{e}_z\}$ is the eigenframe of **Q**: it is thought of as a reference frame fixed in space. The first idea to assess the macroscopic effects of molecular biaxiality was of Freiser [5,6]. Within a mean-field molecular theory, he described a biaxial transition that follows at a lower temperature the uniaxial one, first explained on a molecular basis by Maier and Saupe [7]; while this latter transition is of first order and establishes a positive value of S leaving $T=0$, the new transition is of second order and also makes $T\neq 0$. This theory, however, was not general enough because it did not distinguish the different origins of macroscopic biaxiality: the one related to the distribution of the long molecular axis from the one related to the distribution of the short molecular axes. A more general theory, now a classic, was proposed by Straley [8]. He introduced an additional second-rank order tensor **B** to describe the macroscopic signs of the *intrinsic*, molecular biaxiality. We assume that in the absence of external anisotropic causes, both **Q** and **B** have one and the same eigenframe. Under this assumption, **B** has precisely the same form as **Q** in Eq. (1):

$$\mathbf{B}=S'\left(\boldsymbol{e}_z\otimes\boldsymbol{e}_z-\frac{1}{3}\mathbf{I}\right)+T'(\boldsymbol{e}_x\otimes\boldsymbol{e}_x-\boldsymbol{e}_y\otimes\boldsymbol{e}_y). \tag{2}$$

If both these tensors are employed, a uniaxial phase occurs whenever both **Q** and **B** are uniaxial, that is, whenever both T and T' vanish. A general biaxial state is described by all four scalar parameters S, T, S', and T'. An *extrinsic* biaxiality, which under appropriate external causes could also be exhibited by cylindrically symmetric molecules, is represented by only two scalar order parameters, namely, S and T.

The models of Freiser and Straley have been extensively studied, mostly in attempts to compare the predictions of these with measurements of microscopic biaxiality. Distinguished examples of these studies are in the papers [9–16]. The first comparison with Monte Carlo simulations was presented by Luckhurst and Romano [10]; this was more recently followed by Biscarini *et al.* [13] who explored an impressively large range of molecular biaxialities (see also Ref. [15]). They found the expected sequence of phase transitions: one transition at a higher temperature, which generates a uniaxial state from the isotropic melt, with both S and S' different from zero, and another transition at a lower temperature, where both T and T' are nonzero. In the biaxial phase, they also measured values of S and T' close to unity, always accompanied by very small values of the other two parameters S' and T. The molecular pair potential employed in Ref. [13] is a special case of the one put forward by Straley [8]; it is based on a dispersion forces approximation first applied in Ref. [9], where the molecular biaxiality is frequency independent.

The objective of this paper is to discuss in some detail the expression of Straley's pair potential, which represents the

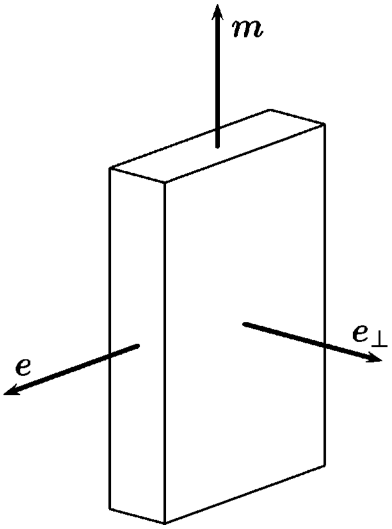

FIG. 1. Schematic description of a biaxial molecule. The unit vector ***m*** represents the long molecular axis, while ***e*** and $\boldsymbol{e}_\perp$ represent the two minor axes.

general nematogenic interaction between molecules with frequency-dependent biaxiality. A systematic analysis does not exist for this general interaction; one wonders whether it would bring some important novel feature. To make such an analysis easier, it is natural to choose a nematogenic compound with a simplified frequency-dependent biaxiality, for which, for instance, the low frequency part would be purely uniaxial and the high frequency one would add the required biaxiality. This search will indeed lead us to unveil a tricritical point in the phase diagram, a feature that is not found within the dispersion forces approximation and that renders our phase diagram very similar to the one discovered by McMillan [17] in his mean-field model for the nematic-to-smectic *A* transition.

The paper is organized as follows. In Sec. II, we review in a tensorial notation the classical Straley interaction potential and we propose criteria that would restrict the choice of its free parameters. This analysis suggests a mean-field model for the biaxial phase, which is studied in Sec. III. Finally, in Sec. IV, we summarize the main conclusions of this paper and comment on the avenues for further research that it opens.

II. BIAXIAL INTERACTIONS

Biaxial molecules can schematically be described as platelets (see Fig. 1). In every platelet, we distinguish the major axis ***m*** from two minor axes ***e*** and $\boldsymbol{e}_\perp$. These are the eigenvectors of any molecular polarizability tensor. The anisotropic part of every molecular biaxial tensor has two traceless, orthogonal components, which are defined as

$$\mathbf{q} := \boldsymbol{m}\otimes\boldsymbol{m} - \frac{1}{3}\mathbf{I}, \tag{3}$$

$$\mathbf{b} := \boldsymbol{e}\otimes\boldsymbol{e} - \boldsymbol{e}_\perp\otimes\boldsymbol{e}_\perp . \tag{4}$$

The tensor **q** is uniaxial around ***m***, while **b** is biaxial: the former has two equal eigenvalues, while the latter has all unequal eigenvalues. If we interpret ***m*** as being the long molecular axis, then **q** is the uniaxial tensor representing the dominant geometric feature of the molecules, while **b** represents their secondary biaxiality. Clearly, this interpretation is purely suggestive as such a simple geometric description of a molecule is too naive. However, it becomes more meaningful when **q** and **b** are employed to describe the uniaxial and biaxial components of molecules in their pairwise interaction. Let two molecules be described by the pairs of tensors $(\mathbf{q},\mathbf{b})$ and $(\mathbf{q}',\mathbf{b}')$. The most general orientational interaction energy V between them, linear in each pair of tensors and invariant under their exchange, takes the form

$$V = -U_0\{\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}'\}, \tag{5}$$

where $U_0 > 0$ is a typical interaction energy and γ and λ are dimensionless parameters. When $\gamma = \lambda = 0$, Eq. (5) represents the interaction energy put forward by Maier and Saupe [7], which depends only on the uniaxial molecular components. When either γ or λ differs from 0, the biaxial components also contribute to the molecular interaction: for $\gamma = 0$ and $\lambda \neq 0$, the biaxial component of one molecule is coupled only with the biaxial component of the other, while for $\gamma \neq 0$, both uniaxial and biaxial components are coupled together. In our tensorial notation, the expression for V in Eq. (5) is precisely the one proposed by Straley [8].

There are special cases of this interaction that deserve notice. First is the one where $\lambda = \gamma^2$. Equation (5) then reduces to

$$V = -U_0(\mathbf{q} + \gamma\mathbf{b})\cdot(\mathbf{q}' + \gamma\mathbf{b}'), \tag{6}$$

as proposed by Luckhurst *et al.* [9]. This formula can easily be interpreted within London's dispersion forces approximation. The anisotropic part of the dielectric polarizability tensor of a biaxial molecule is given by

$$\boldsymbol{\epsilon} = \epsilon_u\mathbf{q} + \epsilon_b\mathbf{b}, \tag{7}$$

where ϵ_u and ϵ_b are the uniaxial and biaxial polarizabilities of the molecule, which depend on the frequency ν of the polarizing field. In the limit where the molecules possess a single absorption frequency ν_a (London approximation), the dispersion forces interaction can be given by the expression in Eq. (6) with γ a function of ν_a (see, for example, Sec. 6.6 of Ref. [18]). However, when the molecules possess more than one absorption frequency, London's theory for dispersion forces breaks down and must be replaced by that of McLachlan (see Refs. [19,20] and Sec. 6.6 of Ref. [18]). Applying this theory, one would, in principle, find for the interaction energy V the general expression in Eq. (5) with γ and λ related to the molecular absorption frequencies. A specific attempt along these lines was made by Bergersen *et al.* [11], who viewed a biaxial molecule as consisting of three orthogonal oscillators with different frequencies. The London approximation model can also be recovered in the presence of dispersion, provided both ϵ_u and ϵ_b remain proportional over the whole frequency range, which is a rather particular situation.

Here, we do not further attempt to find special electrostatic models to justify the expression for V in Eq. (5); we rather seek the conditions to be required on both γ and λ to make this expression reflect some expected qualitative properties. Actually, it was already remarked in Ref. [10] that setting $\lambda=0$ in Eq. (5) would never allow the molecules to reach a stable equilibrium when they all lie parallel to one another. More generally, consider two molecules represented by the pairs $(\mathbf{q},\mathbf{b})$ and $(\mathbf{q}',\mathbf{b}')$, so nearly parallel to one another that the rotation $\mathbf{R}$ that takes the first into the second, for which

$$\mathbf{q}'=\mathbf{R}\mathbf{q}\mathbf{R}^{\mathsf{T}} \quad \text{and} \quad \mathbf{b}'=\mathbf{R}\mathbf{b}\mathbf{R}^{\mathsf{T}} \tag{8}$$

can be represented as

$$\mathbf{R}=\mathbf{I}+\alpha\mathbf{W}+\frac{1}{2}\alpha^2\mathbf{W}^2+o(\alpha^2), \tag{9}$$

where α is the rotation angle and $\mathbf{W}$ is the skew-symmetric tensor associated with the unit vector $\boldsymbol{w}$ along the axis of rotation. By use of Eqs. (8) and (9) in Eq. (5), we arrive at the following expression for the incremental energy δV relative to the state of complete alignment of the two molecules (where $\alpha=0$):

$$\delta V=-\frac{1}{2}U_0\alpha^2\{\mathrm{tr}(\mathbf{W}^2\mathbf{q}^2)-\mathrm{tr}(\mathbf{W}\mathbf{q})^2+2\gamma[\mathrm{tr}(\mathbf{q}\mathbf{b}\mathbf{W}^2) - \mathrm{tr}(\mathbf{q}\mathbf{W}\mathbf{b}\mathbf{W})]+\lambda[\mathrm{tr}(\mathbf{W}^2\mathbf{b}^2)-\mathrm{tr}(\mathbf{W}\mathbf{b})^2]\}+o(\alpha^2). \tag{10}$$

Recalling that $\mathbf{W}\boldsymbol{v}=\boldsymbol{w}\times\boldsymbol{v}$ for all vectors $\boldsymbol{v}$, we can give a more transparent form to Eq. (10) in terms of the components (w_1,w_2,w_3) of $\boldsymbol{w}$ in the eigenframe $\{\boldsymbol{e},\boldsymbol{e}_\perp,\boldsymbol{m}\}$ of both $\mathbf{q}$ and $\mathbf{b}$:

$$\delta V=\frac{1}{2}U_0\alpha^2\{(1+2\gamma+\lambda)w_1^2+(1-2\gamma+\lambda)w_2^2+4\lambda w_3^2\} + o(\alpha^2). \tag{11}$$

It follows from Eq. (11) that δV is positive-definite whenever $\lambda>0$ and $|2\gamma|<1+\lambda$. These inequalities restrict the admissible values of γ and λ to lie within the fan-shaped region depicted in Fig. 2. Further restrictions follow from Eq. (11) if the ground biaxial state represented by the pair potential V in Eq. (5) is *calamitic*, that is, with the long molecular axis $\boldsymbol{m}$ harder to be disoriented than the two minor axes $\boldsymbol{e}$ and $\boldsymbol{e}_\perp$. This physical property has its mathematical counterpart in requiring that the least eigenvalue of the quadratic form for δV in Eq. (11) be associated with the eigenvector $\boldsymbol{w}=\boldsymbol{m}$. This amounts to say that, for a given α, the torque tending to restore the complete alignment between the two interacting molecules is larger when the two long axes are misaligned. Thus, requiring that both $4\lambda<1-2\gamma+\lambda$ and $4\lambda<1+2\gamma+\lambda$, we readily arrive at $2|\gamma|<1-3\lambda$, which corresponds to the shaded triangle in Fig. 2. This small region in the (γ,λ) plane is the one admissible in our study: it is traversed by the parabola $\lambda=\gamma^2$ corresponding to the dispersion forces approximation, the only one extensively studied so far, but it also contains numerous other interaction potentials. In this paper, we explore the λ axis of the admissible triangle. In the following, we set systematically $\gamma=0$ and take λ within the interval $[0,\frac{1}{3}]$: the only pair potential V that this family has in common with that of the dispersion forces approximation is the Maier and Saupe one, which corresponds to the origin of the (γ,λ) plane. Physically, setting $\gamma=0$ in Eq. (5) represents molecules with a special dispersion of the dielectric shape susceptibility: at low frequencies, ϵ_b is zero and ϵ_u would just create a uniaxial nematic phase; at high frequencies, ϵ_u is zero and $\boldsymbol{\epsilon}$ is purely biaxial. Since V is a sum over frequencies of terms like that on the right-hand side of Eq. (6) (see, for instance, Ref. [18]), this is a possible justification for our choice. This choice is as peculiar as the one of the London approximation, since it is possible, though admittedly rather extreme, to imagine a molecule with a purely biaxial $\boldsymbol{\epsilon}$, that is, with $\epsilon_u=0$, at least in some frequency range; the dispersion forces interaction between real molecules should be described by the general Straley interaction.

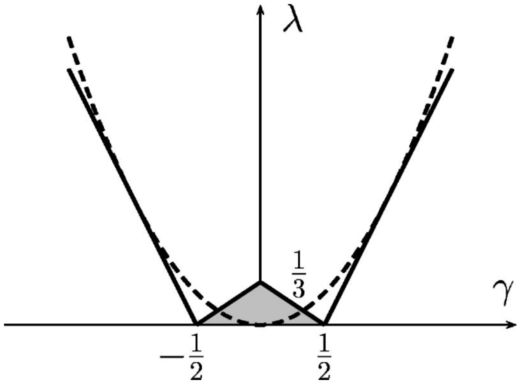

FIG. 2. Admissible values for the dimensionless parameters λ and γ in Eq. (5). The pair-interaction energy V is positive definite in the fan-shaped region. The shaded triangle represents the calamitic ground states. The broken line is the parabola $\lambda=\gamma^2$ corresponding to the dispersion forces approximation; it is tangent to the boundary of the fan-shaped region for $\lambda=1$.

III. MEAN-FIELD MODEL

We consider a homogeneous nematic liquid crystal in the absence of any external field. We assume the molecules to be biaxial and described by the pair of tensors $(\mathbf{q},\mathbf{b})$ introduced in Eqs. (3) and (4). The two independent order tensors employed by Straley [8], $\mathbf{Q}$ and $\mathbf{B}$, are defined as the ensemble averages $\langle\mathbf{q}\rangle$ and $\langle\mathbf{b}\rangle$, respectively. Denoting by $\{\varphi,\vartheta,\psi\}$ the standard Euler angles representing the rotation of an individual molecule with respect to the common eigenframe $\{\boldsymbol{e}_x,\boldsymbol{e}_y,\boldsymbol{e}_z\}$ of $\mathbf{Q}$ and $\mathbf{B}$, which is fixed in space, one readily sees that

$$\boldsymbol{m}=\cos\varphi\sin\vartheta\,\boldsymbol{e}_x+\sin\varphi\sin\vartheta\,\boldsymbol{e}_y+\cos\vartheta\,\boldsymbol{e}_z, \tag{12}$$

$$\boldsymbol{e}=(\cos\psi\cos\varphi\cos\vartheta-\sin\psi\sin\varphi)\boldsymbol{e}_x+(\cos\psi\sin\varphi\cos\vartheta+\sin\psi\cos\varphi)\boldsymbol{e}_y-\cos\psi\sin\vartheta\boldsymbol{e}_z, \tag{13}$$

$$\boldsymbol{e}_\perp=-(\sin\psi\cos\varphi\cos\vartheta+\cos\psi\sin\varphi)\boldsymbol{e}_x-(\sin\psi\sin\varphi\cos\vartheta-\cos\psi\cos\varphi)\boldsymbol{e}_y+\sin\psi\sin\vartheta\boldsymbol{e}_z, \tag{14}$$

and from Eqs. (1) and (2) one then arrives at

$$S=\frac{3}{2}\left\langle\cos^2\vartheta-\frac{1}{3}\right\rangle, \tag{15}$$

$$T=\frac{1}{2}\langle\sin^2\vartheta\cos 2\varphi\rangle, \tag{16}$$

$$S'=\frac{3}{2}\langle\sin^2\vartheta\cos 2\psi\rangle, \tag{17}$$

$$T'=\frac{1}{2}\langle(1+\cos^2\vartheta)\cos 2\varphi\cos 2\psi-2\cos\vartheta\sin 2\varphi\sin 2\psi\rangle, \tag{18}$$

which are essentially the same expressions used in Ref. [8]. To compute these ensemble averages, we need to build a probability distribution function $f=f(\varphi,\vartheta,\psi)$.

There are two ways for the system to become biaxial. If f is isotropic in ψ, but anisotropic in φ, then $T'=0$, whereas $T\neq 0$: this is the *phase* biaxiality produced, for instance, by an anisotropic distribution of cylinderlike molecules under an external field, but which is unlikely to occur spontaneously. On the other hand, a function f isotropic in φ, but anisotropic in ψ, would give $T=0$, but $T'\neq 0$: this is the *intrinsic* biaxiality that would correspond to the natural tendency of biaxial molecules to orient parallel to one another. We expect a spontaneous transition to induce such an intrinsic biaxiality. For all f, the following bounds follow from the admissible ranges of the Euler angles:

$$-\tfrac{1}{2}\leqslant S\leqslant 1,\quad -\tfrac{1}{3}(1-S)\leqslant T\leqslant\tfrac{1}{3}(1-S),$$
$$-(1-S)\leqslant S'\leqslant(1-S),\quad -1\leqslant T'\leqslant 1. \tag{19}$$

We now build the distribution function f by using a mean-field approximation for a particular molecular interaction. We set $\gamma=0$ in Eq. (5) for the pair-interaction potential V and we write the pseudopotential U of a molecule in the mean field described by $\mathbf{Q}$ and $\mathbf{B}$ as

$$U=-U_0(\mathbf{q}\cdot\mathbf{Q}+\lambda\mathbf{b}\cdot\mathbf{B}). \tag{20}$$

We start by taking λ small enough to be interpreted as a perturbation parameter. The asymptotic analysis that we perform below aims at showing quantitatively how this model departs from the classical Maier-Saupe model. The probability density f for a molecular orientation described by the pair $(\mathbf{q},\mathbf{b})$ is given by the Boltzmann distribution

$$f=\frac{1}{Z}\exp[\beta(\mathbf{q}\cdot\mathbf{Q}+\lambda\mathbf{b}\cdot\mathbf{B})], \tag{21}$$

where $\beta:=U_0/k_Bt$, k_B being the Boltzmann constant and t the absolute temperature. In Eq. (21), the partition function Z is defined by

$$Z:=\int_{\mathbb{T}}\exp[\beta(\mathbf{q}\cdot\mathbf{Q}+\lambda\mathbf{b}\cdot\mathbf{B})], \tag{22}$$

where $\mathbb{T}$ is the toroidal manifold $\mathbb{S}^2\times\mathbb{S}^1$ parametrized by the Euler angles, with $\mathbb{S}^n$ the unit sphere in the n-dimensional Euclidean space. Specifically, in Eqs. (21) and (22) $\mathbf{q}\cdot\mathbf{Q}$ and $\mathbf{b}\cdot\mathbf{B}$ are expressed in terms of the Euler angles $\{\varphi,\vartheta,\psi\}$ and the scalar order parameters (S,T,S',T') as

$$\mathbf{q}\cdot\mathbf{Q}=S\left(\cos^2\vartheta-\frac{1}{3}\right)+T\sin^2\vartheta\cos 2\varphi, \tag{23}$$

$$\mathbf{b}\cdot\mathbf{B}=S'\sin^2\vartheta\cos 2\psi+T'[(1+\cos^2\vartheta)\cos 2\varphi\cos 2\psi-2\cos\vartheta\sin 2\varphi\sin 2\psi]. \tag{24}$$

Moreover, the area measure on $\mathbb{T}$ in Eq. (22) is $\sin\vartheta d\varphi d\vartheta d\psi$.

Clearly, since f depends on the averages $\mathbf{Q}$ and $\mathbf{B}$, it must obey the following compatibility conditions:

$$\mathbf{Q}=\int_{\mathbb{T}}f\mathbf{q},\quad \mathbf{B}=\int_{\mathbb{T}}f\mathbf{b}. \tag{25}$$

Following Refs. [5,6], we introduce the potential

$$F(\mathbf{Q},\mathbf{B}):=U_0\left\{\frac{1}{2}(\mathbf{Q}\cdot\mathbf{Q}+\lambda\mathbf{B}\cdot\mathbf{B})-\frac{1}{\beta}\ln\frac{Z}{8\pi^2}\right\}, \tag{26}$$

which has the property of attaining its extrema precisely at those order tensors $\mathbf{Q}$ and $\mathbf{B}$ that comply with the compatibility conditions (25). At equilibrium, F can be interpreted as the free energy per molecule of the system. As remarked in Ref. [21], arriving at the free energy out of equilibrium F_{neq} requires much more care; however, F and F_{neq} possess precisely the same stationary points, which is what matters here. When expressed in terms of the scalar order parameters (S,T,S',T'), the potential F will be denoted by $F^*(S,T,S',T')$.

We first show that our model encompasses that of Maier and Saupe. We set $\lambda=0$ in Eq. (26): F^* is now a function of S and T only, which will more appropriately be denoted by F_0^*. By expanding Z up to the 12th order in T, we checked that the minimizers of F_0^* can only occur for $T=0$ at precisely the same values of S obtained by Maier and Saupe [7]. $S=0$ for $\beta\leqslant\beta_c\approx 6.81$, while at $\beta=\beta_c$ a first-order isotropic-to-nematic transition takes place which establishes $S=S_c\approx 0.43$. We do not study in any further detail this classical model for uniaxial nematics; we only heed that F_0^* attains its minimum at $S=S_0(\beta)$ and $T=0$, with S_0 a function increasing from S_c to unity as β ranges from β_c to infinity, which satisfies the inequality

$$S_0(\beta)\geqslant\frac{1}{4}\left(1+3\sqrt{1-\frac{20}{3\beta}}\right)\quad\text{for all}\quad\beta\geqslant\beta_c. \qquad (27)$$

This estimate is easily obtained by requiring that the second derivative of F_0^* with respect to S at $T=0$, which on all stationary points of F_0^* is quadratic in S, be positive at $S=S_0$. Here, the obvious conclusion is that for purely uniaxial interactions, no transition to a phase biaxiality is possible.

We now set $\lambda>0$ to enforce a biaxial interaction between molecules. We take λ small enough, so as to justify an expansion of F^* in λ on a firmer ground than the expansion of F_0^* in T. From Eq. (26), we arrive at the following expression for F^* near the critical point $(S_0,0)$ of F_0^*:

$$F^*(S_0,0,S',T') = F_0^*(S_0,0)+U_0\lambda\left\{\left(\frac{1}{3}+\frac{\lambda}{4}-\frac{1}{6}(1-S_0)\beta\lambda\right)S'^2 + \left(1+\frac{\lambda}{8}-\frac{1}{12}(5+7S_0)\beta\lambda\right)T'^2\right\}+O(\lambda^4). \qquad (28)$$

It is apparent from Eq. (28) that the origin of the (S',T') plane would become unstable towards perturbations of S' and T' as soon as

$$\lambda>\lambda_{S'}:=\frac{4}{2(1-S_0)\beta-3},$$

$$\lambda>\lambda_{T'}:=\frac{24}{2(5+7S_0)\beta-3}, \qquad (29)$$

respectively. By use of inequality (27), it is easily checked that $\lambda_{T'}<\lambda_{S'}$ for all $\beta\geqslant\beta_c$, and so in Eq. (28) T'^2 grows systematically before S'^2 upon increasing λ. Moreover, for a given λ, a good estimate of the critical value β_c' of β at which this secondary transition takes place can be obtained from the inequality

$$\lambda\geqslant\lambda_0(\beta):=\frac{16}{\left(9+7\sqrt{1-\frac{20}{3\beta}}\right)\beta-2}>\lambda_{T'}, \qquad (30)$$

where λ_0 is a strictly decreasing function that decays like $1/\beta$ at infinity. When λ is sufficiently small, the biaxial state that is established for $\beta>\beta_c'$ is characterized by having $S=S_0(\beta)$, $T=0$, $S'=0$, and $T'\neq 0$. Within this limit, only two parameters are thus necessary to describe the transitions leading the system to this state: S for the first (isotropic to uniaxial) and T' for the second (uniaxial to biaxial). It is shown below by numerical computations that for larger values of λ, both T and S' are not exactly zero: they grow whenever T' does, though remaining some orders of magnitude smaller. Yet the biaxial phase is primarily described by the two prevailing order parameters S and T', pertaining to the two different tensors **Q** and **B**.

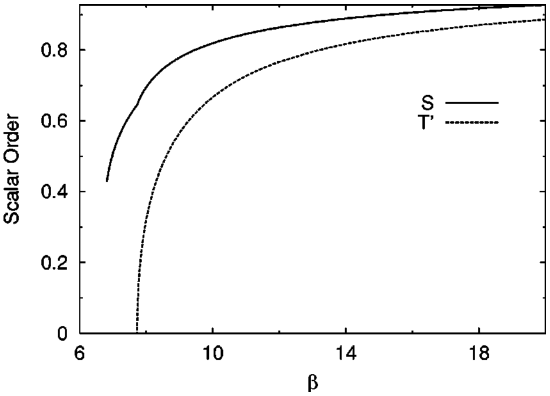

FIG. 3. Order parameters S and T' versus inverse temperature β for $\lambda=1/6$. The second-order transition from uniaxial to biaxial nematic occurs at $\beta=\beta_c'\approx 7.72$.

So far in our analysis, λ has been regarded as a perturbation parameter. By solving numerically the compatibility conditions (25), we now extend the validity of our model to values of λ in the range $[0,\frac{1}{3}]$. Choosing, for instance, $\lambda=\frac{1}{6}$, we plot in Fig. 3 the temperature evolution of the two dominant order parameters S and T'. For $\beta=\beta_c$, we observe the first-order isotropic-to-uniaxial transition, followed at lower temperatures by a saturation of S towards 1. For $\beta=\beta_c'>\beta_c$, we observe the second-order uniaxial-to-biaxial transition, followed at lower temperatures by a saturation of T' towards 1. We do not reproduce in this plot the graphs for S' and T, which arise from 0 at $\beta=\beta_c'$, because their maximum values remain five orders of magnitude smaller than S and T'. The behavior shown by Fig. 3 is indeed typical for all values of λ up to $\lambda_t\approx 0.20$, above which the second-order transition becomes a first-order one. Figure 4 shows in the plane $(\lambda,1/\beta)$ the phase diagram predicted by our model. Following Griffiths's notation [22], we represent the first-order transitions with a solid line and the second-order transitions with a broken line: the point where they meet is the *tricritical* point $(\lambda_t,1/\beta_t)$, with $\beta_t\approx 7.07$. The same se-

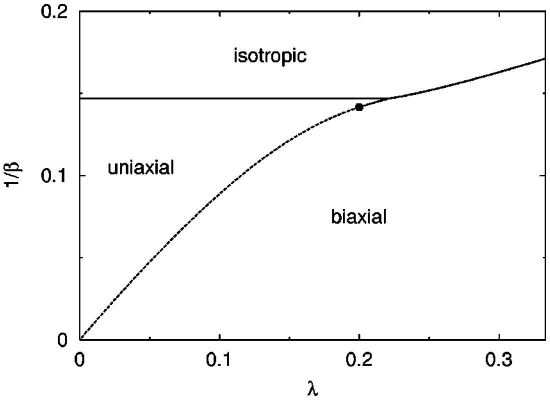

FIG. 4. Phase diagram showing the reduced temperature $1/\beta$ versus the biaxiality parameter λ. The solid line represents the first-order transitions, while the broken line represents the second-order transitions. The tricritical and triple points occur for $\lambda_t\approx 0.20$ and $\beta_t\approx 7.07$, and $\lambda_c\approx 0.22$ and $\beta_c\approx 6.81$, respectively.

quence of phases exhibited in Fig. 3 occurs until $\lambda=\lambda_c \approx 0.22$; for $\lambda>\lambda_c$, there is a direct first-order transition from the isotropic to the nematic biaxial phase, without any intermediate uniaxial phase. The three phases coexist at the triple point $(\lambda_c, 1/\beta_c)$. The phase diagram reproduces the expected behavior: upon increasing λ, the biaxial phase becomes more and more favored.

The resemblance between this phase diagram and the one obtained by McMillan [17] within his mean-field model for smectic *A* is remarkable. McMillan's diagram exhibits a tricritical point where the phase transition between the uniaxial and the smectic phase ceases to be of second order and becomes first order upon increasing the parameter that in the pseudopotential promotes the formation of smectic layers. To make this comparison more quantitative, we note that at the tricritical point in our diagram, the temperature t_{UB} of the uniaxial-to-biaxial transition is related to the temperature t_{IN} of the isotropic-to-nematic transition through $t_{UB}/t_{IN} = \beta_c/\beta_t \approx 0.96$, while at the tricritical point in McMillan's diagram the temperature t_{NA} of the nematic-to-smectic transition is given by $t_{NA}/t_{IN} \approx 0.87$. The existence of a tricritical point in the phase diagram for biaxial nematics is a distinctive feature predicted by our model. To our knowledge, all other microscopic models, mainly based on the dispersion forces approximation, predict a Landau critical point (see, for example, Refs. [8,23–25]), where, in Alben's terminology, an ''accidental'' second-order phase transition occurs. This is the single point where the second-order lines separating the biaxial phase from the prolate and oblate uniaxial phases, respectively, meet the first-order line, separating both uniaxial phases from the isotropic one: a direct transition from the isotropic to the biaxial phase occurs there. This point, which in our phrasing of the dispersion forces approximation appears for $\lambda=\frac{1}{3}$, is not present in our diagram because the model we employ is an extension of Maier and Saupe's model with $S>0$, and so oblate uniaxial phases are excluded from the start.

Positing a complete macroscopic theory for biaxial nematics that would describe both phase and intrinsic biaxialities first requires writing the free energy in terms of both order tensors **Q** and **B**. This would indeed be the central feature of the Landau theory near equilibrium. An approximate expression for the Landau potential can be obtained by expanding in powers of β the free energy in Eq. (26). To within terms in β^4, F reads as

$$\begin{aligned} F(\mathbf{Q},\mathbf{B}) = U_0\Biggl\{ & \frac{1}{15}\left[\left(\frac{15}{2}-\beta\right)\operatorname{tr}\mathbf{Q}^2 - \frac{4}{21}\beta^2\operatorname{tr}\mathbf{Q}^3 \right. \\ & \left. + \frac{1}{105}\beta^3(\operatorname{tr}\mathbf{Q}^2)^2\right] + \frac{1}{5}\lambda\beta\left(\frac{5}{2\beta}-\lambda\right)\operatorname{tr}\mathbf{B}^2 \\ & + \frac{4}{35}\lambda^2\beta^2\operatorname{tr}\mathbf{Q}\mathbf{B}^2 + \frac{1}{175}\lambda^2\beta^3\left[\frac{11}{3}(\operatorname{tr}\mathbf{Q}\mathbf{B})^2\right. \\ & \left. - 6\operatorname{tr}\mathbf{Q}^2\mathbf{B}^2 + \lambda^2(\operatorname{tr}\mathbf{B}^2)^2\right]\Biggr\}. \end{aligned} \tag{31}$$

For $\lambda=0$, the expression for F in Eq. (31) coincides with the one obtained in Ref. [26] for Maier and Saupe's model. Equation (31) is accordingly exposed to the same criticism suffered by Ref. [26] in Ref. [21], where a systematic approximation to the nonequilibrium free energy F_{neq} in the vicinity of the equilibrium points correctly predicted by F was proposed. Though the expression in Eq. (31) could be quantitatively inaccurate, it retains some qualitative features of F_{neq} worth mentioning, as we learn from the simpler analog in Ref. [26]. It predicts that when λ is sufficiently small and β is not too large, the free energy F attains its minimum in a uniaxial phase with $\mathbf{Q}\neq\mathbf{0}$ and $\mathbf{B}=\mathbf{0}$. The terms $\operatorname{tr}\mathbf{QB}$, $\operatorname{tr}\mathbf{B}^3$, $\operatorname{tr}\mathbf{Q}^2\mathbf{B}$, $\operatorname{tr}\mathbf{Q}^3\mathbf{B}$, and $\operatorname{tr}\mathbf{QB}^3$, which would be allowed in Eq. (31) by the mere requirement of invariance under rotations, are indeed missing because they would fail to be invariant under the symmetry transformation for the pseudopotential defined by $(\mathbf{q},\mathbf{b})\mapsto(\mathbf{q},-\mathbf{b})$ and $(\mathbf{Q},\mathbf{B})\mapsto(\mathbf{Q},-\mathbf{B})$. The explicit temperature dependence of the coefficients in Eq. (31) should not be taken literally, but their signs are meaningful: in a theory *à la* Landau, the coefficients of Eq. (31) are to be replaced by phenomenological parameters retaining the same sign. The purely phenomenological theory outlined in Refs. [27,28], once restricted up to the fourth order in the scalar order parameters S, S', T, and T', proposed only four invariants in the free energy out of the at least eight possible.

We close the analysis of our model by comparing it with the mean-field model for biaxial phases put forward by Freiser [5,6]. Assuming that the anisotropic part of the molecular polarizability $\boldsymbol{\epsilon}$ be represented by Eq. (7), Freiser writes the pair potential as $V=-V_0\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}'$, with $V_0>0$, but he takes **Q** as $\langle\boldsymbol{\epsilon}\rangle$ instead of $\langle\mathbf{q}\rangle$, and so the internal energy turns out to be quadratic in **Q** only. Freiser's model has been fully solved in Refs. [24,23]. The phase diagrams found there are very similar to the one shown by Straley [8] for a special relation between the parameters γ and λ in Eq. (5); they all present a Landau point, but no tricritical point. Mathematically, Freiser's model can be recovered as a special case of ours by enforcing the constraint $\mathbf{Q}=\mathbf{B}$ and by setting $\lambda=\epsilon_b/\epsilon_u$ in Eq. (20). This actually forces T and T' to coincide. The apparent simplification coming from merging T' and S in the same tensor is eventually misleading because they do belong to two tensors with different physical origins.

IV. CONCLUSIONS

All microscopic models describing the onset of biaxial nematic phases are based on intermolecular dispersion forces. The interaction potential is taken to be proportional to the inner product of the two tensors representing the anisotropic dielectric susceptibilities. In the presence of frequency dispersion, the interaction is the sum of each frequency component. For real molecules, the interaction potential has then the complicated form put forward by Straley on the basis of pure symmetry arguments. The first idealization of this model, based on the London approximation, has been extensively discussed in the past. This case corresponds to the maximum coupling between uniaxial and biaxial molecular susceptibilities, assumed to remain proportional over the whole frequency range. In this work, we have chosen another, orthogonal avenue, the one that presents the least possible coupling between uniaxial and biaxial susceptibilities. Real molecules are expected to present an intermediate behavior between these two idealizations. Along this line of thought, we have presented a simple mean-field model for the uniaxial-to-biaxial transition in nematic liquid crystals, which identifies two dominant scalar order parameters. It explains why the single-order tensor description first employed by Freiser is of a limited use, despite its apparent success. It suggests an approximate expression for the macroscopic free energy in terms of the relevant invariants of the two order tensors actually needed to describe the behavior of biaxial nematics. The structure of this potential is the theoretical premise for a complete macroscopic theory able to describe the interplay between phase and intrinsic biaxialities.

Our model has revealed the existence of a tricritical point in the phase diagram, which, to our knowledge, cannot be retraced in any other molecular model for biaxial liquid crystals, though it is fully compatible with the Landau theory [29]. This result raises a number of questions. First, it suggests a bifurcation analysis to classify all Landau potentials compatible with this feature, whenever only two scalar order parameters are dominant, in the spirit of the theory developed in Ref. [30]. Moreover, since in our model the tricritical point is projected on the λ axis of the admissible triangle in Fig. 2, the question arises whether for $\gamma \neq 0$ the tricritical point still exists and how its projection wanders in the (γ,λ) plane. Since no tricritical point is associated with the dispersion forces approximation, which predicts a Landau point at $\lambda = \frac{1}{3}$, a sensible conjecture is that there is a path of tricritical points projected on the (γ,λ) plane that joins the point $(0,\lambda_t)$ to the two symmetric points at $\lambda = \frac{1}{3}$ on the parabola $\lambda = \gamma^2$. These issues will be addressed in near future.

We are aware of the fact that arguments different from merely resorting to the dispersion forces approximation could justify a choice of dominant order parameters, which is consistent with setting $\lambda = \gamma^2$ in the molecular pair potential, even without ever considering the latter (see, for example, Ref. [31]). However, the *scenario* unveiled by the study of our limiting model with $\gamma = 0$ and $\lambda \neq 0$, which is also likely to persist for $\lambda \approx \gamma^2$, makes somewhat singular all analyses based on, or equivalent to, setting precisely $\lambda = \gamma^2$. Further studies are needed to explore properly how the phase diagram evolves when two extreme situations compatible with the model molecular interaction of Straley are bridged together, that is, the London approximation, where the two biaxial order parameters show maximum coupling, and the approximation studied in this paper, where the order parameters show minimum coupling.

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