

Tricritical points in biaxial liquid crystal phases

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We further pursue the analysis of a mean-field model recently proposed by Sonnet *et al.* [Phys. Rev. E **67**, 061701 (2003)] to describe nematic biaxial phases. This model, which is based on a simplified version of Straley's pair potential, is characterized by the prediction of a tricritical point along the transition line between uniaxial and biaxial phases. We show that the same model predicts another tricritical point, but along the line of the direct isotropic-to-biaxial transition. Our prediction is quantitative, as it stems from an analytical criterion for tricriticality.

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I. INTRODUCTION

The search for thermotropic biaxial liquid crystals has recently received a fresh impetus from new experimental evidence that appears to support their existence [1–3]. As remarked by Luckhurst, “The announcement has created considerable excitement, for it opens up new areas of both fundamental and applied research. It seems that a Holy Grail of liquid-crystal science has been found” [4].

The very existence of biaxial liquid crystal phases finds its justification in the intimate structure of liquid crystal molecules, which are indeed more similar to flat platelets than to slender rods. Thermal fluctuations prevent this microscopic symmetry from emerging at the macroscopic scale, if rotations of molecules about their long axis are efficient enough to create an effective rotationally symmetric molecule able to replace the actual flat molecule in its interactions with the neighbors. If no remains are left at the macroscopic scale of the peculiar microscopic symmetry, no thermotropic biaxial phase can be expected to result from collective molecular cooperation. Only if molecular rotations are somewhat hampered by mutual molecular interactions is there hope that a biaxial phase manifests itself.

The first theoretical prediction of biaxial nematics is unanimously attributed to Freiser [5,6]. A broad review of both theoretical and experimental attempts made to unveil the secrets of these elusive phases can be found in Ref. [7]. More recently, a mean-field model for biaxials was proposed that departs from most theoretical avenues taken in the past [8]. This model predicted a *tricritical* point in the transition from uniaxial to biaxial nematics, that is, a point where the transition changes from first to second order. The existence of this point, which was the major novelty introduced in the theory of biaxial phases in Ref. [8], has so far been con-

firmed by both a Monte Carlo simulation [9] and an experimental study [10].

The occurrence of a tricritical point in the phase diagram of biaxial nematics calls for a more systematic study to identify all such points and the sides of the transition lines that indeed correspond to second-order phase transitions. This paper is devoted to such a study.

The paper is organized as follows. In Sec. II, we recall the model for biaxial phases employed here. In Sec. III, we digress slightly from the main development of the paper to illustrate an analytical criterion to find tricritical points in a setting sufficiently general to encompass our biaxial model as a special case. In Sec. IV, with the aid of the criterion illuminated in Sec. III, we predict the existence of a tricritical point for biaxial liquid crystals in a range of parameters not yet explored. Finally, in Sec. V, we draw the main conclusion of this paper and comment on the perspectives that it opens. For completeness, in a closing Appendix, we also contrast the criterion presented here with the known extensions [11–13] of Griffiths' criterion [14,15].

II. MODEL FOR BIAXIAL NEMATICS

In Ref. [8], Straley's molecular pair potential [16] has been studied beyond the range of validity of both London's dispersion force approximation and Freiser's model [5,6], which are intimately connected to one another. The general form of Straley's pair potential V can be expressed by representing each interacting molecule by a pair of traceless, symmetric, second-rank tensors (\mathbf{q}, \mathbf{b}) , where

$$\mathbf{q} := \mathbf{m} \otimes \mathbf{m} - \frac{1}{3} \mathbf{I} \quad (1)$$

is purely uniaxial around the long molecular axis \mathbf{m} , and

$$\mathbf{b} := \mathbf{e} \otimes \mathbf{e} - \mathbf{e}_\perp \otimes \mathbf{e}_\perp \quad (2)$$

is fully biaxial and orthogonal to \mathbf{q} . The orthonormal basis $\{\mathbf{e}, \mathbf{e}_\perp, \mathbf{m}\}$ is the eigenframe of any molecular polarizability

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tensor. Letting (\mathbf{q}, \mathbf{b}) and $(\mathbf{q}', \mathbf{b}')$ represent two interacting molecules, we write V as

$$V = -U_0\{\mathbf{q} \cdot \mathbf{q}' + \gamma(\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}'\}, \quad (3)$$

where $U_0 > 0$ is a typical interaction energy, and λ and γ are model parameters.

Macroscopically, the liquid crystal is described by two order tensors, both defined as ensemble averages:

$$\mathbf{Q} := \langle \mathbf{q} \rangle, \quad \mathbf{B} := \langle \mathbf{b} \rangle.$$

Under the assumption that \mathbf{Q} and \mathbf{B} have a common eigenframe $\{\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\}$, which is plausible in the absence of any external distorting cause, they can be represented as follows:

$$\mathbf{Q} = S \left(\mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3} \mathbf{I} \right) + T (\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y), \quad (4)$$

$$\mathbf{B} = S' \left(\mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3} \mathbf{I} \right) + T' (\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y), \quad (5)$$

where S, T, S', T' are the order parameters of the system. \mathbf{Q} represents the average quadrupolar distribution of the long molecular axis: its degree of biaxiality measured by T reflects the lack of axial symmetry in the orientational distribution function. \mathbf{B} reflects on a macroscopic scale the intrinsic biaxiality of molecules and the role it plays in the molecular interaction: like \mathbf{Q} , in general, \mathbf{B} has both a uniaxial and a biaxial component. S is precisely Maier-Saupe's order parameter [17]: when T, S' , and T' all vanish, the resulting phase is purely uniaxial. We would call a phase uniaxial even when only S and S' do not vanish, though the origin of S' is to be retraced in the intrinsic molecular biaxiality. Similarly, T and T' express degrees of biaxiality of two different origins.

In the mean-field approximation adopted in Ref. [8], a single molecule experiences the pseudopotential

$$U(\mathbf{q}, \mathbf{b}) = -U_0\{\mathbf{Q} \cdot \mathbf{q} + \gamma(\mathbf{Q} \cdot \mathbf{b} + \mathbf{B} \cdot \mathbf{q}) + \lambda \mathbf{B} \cdot \mathbf{b}\}. \quad (6)$$

Accordingly, the partition function Z and the free energy \mathcal{F} are

$$Z(\mathbf{Q}, \mathbf{B}, \beta, \lambda, \gamma) = \int_{\mathbb{T}} \exp\{\beta[\mathbf{Q} \cdot \mathbf{q} + \gamma(\mathbf{Q} \cdot \mathbf{b} + \mathbf{B} \cdot \mathbf{q}) + \lambda \mathbf{B} \cdot \mathbf{b}]\}, \quad (7)$$

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

where \mathbb{T} is the manifold described by all possible molecular orientations $\{\mathbf{e}, \mathbf{e}_\perp, \mathbf{m}\}$, $\beta := U_0 / \kappa_B t$, κ_B is the Boltzmann constant, and t is the absolute temperature. In Ref. [8], the case where $\gamma=0$ and λ ranges in the interval $[0, \frac{1}{3}]$ was extensively considered and a tricritical point was discovered in the phase diagram. More precisely, it was shown that for small enough values of λ the classical Maier-Saupe first-order transition from the isotropic phase is followed, at a large enough

value of β , by a second-order transition to a biaxial phase characterized by $T' \neq 0$ and by both T and S' almost vanishing. This scenario changes qualitatively when λ grows: the transition to the biaxial phase becomes first order, as shown by solving numerically the equilibrium equations, thus disclosing a tricritical point.

Although, strictly speaking, all admissible states are described by four scalar order parameters, two, namely, T and S' , can be set equal to zero at all equilibrium phases [8], and the free energy \mathcal{F} in Eq. (8) turns out to be a function of S and T' only, even in T' . Henceforth we shall call

$$\mathcal{F} = \mathcal{F}(S, T', \beta, \lambda) \quad (9)$$

the function obtained from Eq. (8) by setting $\gamma=0$ and $S=T'=0$.

It would be desirable to apply an analytical criterion to find all tricritical points in the phase diagram associated with the free energy in Eq. (9) for all positive β and λ . The classical criterion for tricriticality put forward by Griffiths [14,18] applies only to free energies depending on a single order parameter. Extensions of this criterion to free energies with more than one order parameter have already been proposed in the literature [11–13], under the assumption that one order parameter is dominant and all others depend on it. For clarity, in the following section we derive a criterion appropriate to our case, where the two order parameters are in principle independent of one another. In Appendix B we show for completeness that the criterion known in the case of a single dominant order parameter agrees with ours.

III. TRICRITICALITY CRITERION

Here we consider a smooth free-energy function \mathcal{F} as in Eq. (9), not necessarily given in the form of Eq. (8). Of this latter, we only retain the following symmetry property

$$\mathcal{F}(S, T', \beta, \lambda) = \mathcal{F}(S, -T', \beta, \lambda), \quad (10)$$

which makes equilibria with $T'=0$ the natural candidates for states whence a second-order phase transition could develop.

At equilibrium, for given β and λ , the order parameters of the system solve the equations

$$\frac{\partial \mathcal{F}}{\partial S}(S, T', \beta, \lambda) = 0, \quad (11)$$

$$\frac{\partial \mathcal{F}}{\partial T'}(S, T', \beta, \lambda) = 0. \quad (12)$$

These equations may possess more than a single root (S, T') , each of which represents an equilibrium phase. We call *locally stable* a phase where \mathcal{F} attains a relative minimum and *globally stable* a phase where \mathcal{F} attains its absolute minimum. We assume that the system always admits a globally stable phase. First let λ_0 be given. Suppose that for all $\beta > 0$ there is an equilibrium phase described by $S=S_0(\beta, \lambda_0)$ and $T'=0$. Conventionally, we say that $(S_0, 0)$ represents a *reference state* for the system. It may represent a stable phase of the system and it may not: it could be any equilibrium

state of the system whose vicinity is worth exploring. We denote by $[H_0]$ the Hessian matrix of \mathcal{F} at the point $(S_0, 0)$. By the symmetry requirement (10), $[H_0]$ is diagonal, and its two eigenvalues are given by

$$\Sigma_S(\beta, \lambda_0) := \frac{\partial^2 \mathcal{F}}{\partial S^2}(S_0(\beta, \lambda_0), 0, \beta, \lambda_0), \quad (13)$$

$$\Sigma_{T'}(\beta, \lambda_0) := \frac{\partial^2 \mathcal{F}}{\partial T'^2}(S_0(\beta, \lambda_0), 0, \beta, \lambda_0). \quad (14)$$

Our strategy will be to look for other equilibrium phases near a given reference state and, if there are any, to see which is likely to be locally stable. The success of this strategy will clearly depend on the choice of the reference state. We expand the free energy \mathcal{F} in power series about $(S_0, 0)$:

$$\begin{aligned} \mathcal{F}(S_0 + \delta S, T') &= \mathcal{F}(S_0, 0) + F_1 T'^2 + F_2 T'^4 + F_3 T'^2 \delta S \\ &+ F_4 (\delta S)^2 + F_5 (\delta S)^4 + F_6 T'^2 (\delta S)^2 + F_7 (\delta S)^3 \\ &+ O(5), \end{aligned} \quad (15)$$

where use has been made again of the symmetry requirement (10). The coefficients $\{F_j\}_{j=1,\dots,7}$ are related to the partial derivatives of \mathcal{F} with respect to S and T' at the reference state: they are all functions of (β, λ_0) . In particular, also by Eqs. (13) and (14),

$$F_1 := \frac{1}{2} \Sigma_{T'}(\beta, \lambda_0), \quad (16)$$

$$F_2 := \frac{1}{24} \left(\frac{\partial^4 \mathcal{F}}{\partial T'^4} \right)_{(S_0, 0)}, \quad (17)$$

$$F_3 := \frac{1}{2} \left(\frac{\partial^3 \mathcal{F}}{\partial T'^2 \partial S} \right)_{(S_0, 0)}, \quad (18)$$

$$F_4 := \frac{1}{2} \Sigma_S(\beta, \lambda_0). \quad (19)$$

If there exist equilibrium phases near the reference state, they can be found by requiring the function in Eq. (15) to be stationary, that is, by solving the equations

$$F_3 T'^2 + 2F_4 \delta S + 4F_5 (\delta S)^3 + 2F_6 T'^2 \delta S + 3F_7 (\delta S)^2 = 0, \quad (20)$$

$$F_1 T' + 2F_2 T'^3 + F_3 T' \delta S + F_6 T' (\delta S)^2 = 0. \quad (21)$$

Under the assumption that $T' \neq 0$, to the lowest approximation, these equations reduce to the following linear system:

$$\begin{pmatrix} 2F_4 & F_3 \\ F_3 & 2F_2 \end{pmatrix} \begin{pmatrix} \delta S \\ T'^2 \end{pmatrix} = \begin{pmatrix} 0 \\ -F_1 \end{pmatrix}. \quad (22)$$

It is apparent from Eq. (22) that an additional single-equilibrium phase fails to exist whenever

$$\Delta F := 4F_2 F_4 - F_3^2 = 0. \quad (23)$$

This condition actually identifies the *singular line* in the

plane (β, λ) . More properly, we should momentarily think of λ as being freed from the assigned value λ_0 and of $(S_0(\beta, \lambda), 0)$ as the continuation in λ of the equilibrium solution $(S_0(\beta, \lambda_0), 0)$. Thus, Eq. (23) explicitly becomes

$$\begin{aligned} \Delta F(\beta, \lambda) &:= \frac{\partial^4 \mathcal{F}}{\partial T'^4}(S_0(\beta, \lambda), 0, \beta, \lambda) \frac{\partial^2 \mathcal{F}}{\partial S^2}(S_0(\beta, \lambda), 0, \beta, \lambda) \\ &- 3 \left(\frac{\partial^3 \mathcal{F}}{\partial T'^2 \partial S}(S_0(\beta, \lambda), 0, \beta, \lambda) \right)^2 = 0. \end{aligned} \quad (24)$$

When (β, λ_0) does not belong to the singular line, the solution to Eq. (22) is *admissible*, that is, it delivers $T'^2 > 0$, only if

$$F_1 F_4 \Delta F < 0. \quad (25)$$

Moreover, the equilibrium phase is close to the reference state $(S_0, 0)$, if F_1 is infinitesimal. For this reason we choose the reference state $(S_0, 0)$ such that (β, λ_0) is near the *critical line*, which is defined by the conditions

$$\Sigma_{T'}(\beta, \lambda) := \frac{\partial^2 \mathcal{F}}{\partial T'^2}(S_0(\beta, \lambda), 0, \beta, \lambda) = 0, \quad (26)$$

$$\Sigma_S(\beta, \lambda) := \frac{\partial^2 \mathcal{F}}{\partial S^2}(S_0(\beta, \lambda), 0, \beta, \lambda) > 0, \quad (27)$$

where the latter ensures that the equilibrium phase $(S_0(\beta, \lambda), 0)$ is locally stable against all perturbations in the S order parameter. When (β, λ_0) lies precisely on the critical line, F_1 vanishes in Eq. (22) and the equilibrium phases reduce to the reference state: all equilibrium solutions corresponding to the critical line can be thought of as states whence additional equilibria are to bifurcate. Choosing (β, λ_0) near the critical line captures the bifurcation onset, and so makes successful the strategy of finding more equilibrium phases near the reference state.

As a consequence of inequality (27), F_4 is positive in Eq. (20) and this reduces the admissibility condition (25) to

$$F_1 \Delta F < 0. \quad (28)$$

This inequality is central in the following stability analysis. At the lowest approximation, the Hessian matrix of \mathcal{F} computed at $(S_0 + \delta S, T')$, where $(\delta S, T')$ solves Eq. (22), is

$$[H] = \begin{pmatrix} 2F_4 & 2F_3 T' \\ 2F_3 T' & 2F_1 + 12F_2 T'^2 + 2F_3 \delta S \end{pmatrix}. \quad (29)$$

Since $F_4 > 0$, the sign of $\det[H]$ suffices to characterize the local stability of $(S_0 + \delta S, T')$:

$$\det[H] = 4F_1 F_4 + 6T'^2 (4F_2 F_4 - F_3^2) = -8F_1 F_4. \quad (30)$$

Moreover, within the same approximation, the energy difference reads as

$$\Delta \mathcal{F} := \mathcal{F}(S_0 + \delta S, T') - \mathcal{F}(S_0, 0) = -\frac{F_1^2 F_4}{\Delta F}. \quad (31)$$

Our assert is that the intersection between the critical and the singular lines, if not empty, is constituted of tricritical

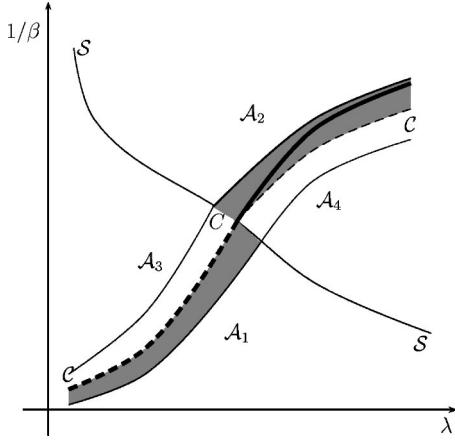


FIG. 1. The tricritical point C is identified as the intersection between the critical line C and the singular line S in the plane $(\lambda, 1/\beta)$. $\mathcal{A}_1 \cup \mathcal{A}_2$ is the admissible set, where there is an equilibrium phase near the reference state. The heavy dashed line is a second-order transition line, while the heavy solid line is a first-order transition line, whose existence is predicted by the arguments developed in the text.

points, which represent states where the character of a phase transition changes from first to second order. In Fig. 1, both the critical line C and the singular line S are represented in the plane $(\lambda, 1/\beta)$. We assume that these curves cross at the point C . ΔF vanishes along S , and $\Sigma_{T'}$ vanishes along C . Near C , a tubular neighborhood of C is divided into four parts by S and C , which we call \mathcal{A}_1 , \mathcal{A}_2 , \mathcal{A}_3 , and \mathcal{A}_4 . For definiteness, we assume that $\Sigma_{T'} > 0$ in $\mathcal{A}_2 \cup \mathcal{A}_3$ and $\Sigma_{T'} < 0$ in $\mathcal{A}_1 \cup \mathcal{A}_4$, while $\Delta F > 0$ in $\mathcal{A}_1 \cup \mathcal{A}_3$ and $\Delta F < 0$ in $\mathcal{A}_2 \cup \mathcal{A}_4$. By inequality (28), $\mathcal{A}_1 \cup \mathcal{A}_2$ is the *admissible set*, that is, the set where there are equilibrium phases near the reference state. By Eqs. (30) and (31), in \mathcal{A}_1 the additional equilibrium phase is locally stable since $\det[H] > 0$ and it possesses less energy than the reference state since $\Delta \mathcal{F} < 0$. Moreover, since there $\Sigma_{T'} < 0$, the reference state has become unstable. Clearly, in \mathcal{A}_1 a further stable phase bifurcates from the reference state. Similarly, in \mathcal{A}_2 $\det[H] < 0$ and $\Delta \mathcal{F} > 0$, while $\Sigma_{T'} > 0$. This means that the equilibrium phase represents an unstable equilibrium with more energy than the reference state, while the reference state is still stable. Here no bifurcation occurs. Away from the admissible set, the reference state is not accompanied by any other equilibrium phase in its vicinity. The reference state itself is locally stable in \mathcal{A}_3 and unstable in \mathcal{A}_4 . Since here we assume that a globally stable phase always exists for the system, when the parameters are chosen in \mathcal{A}_4 , this phase must lie away from the reference state. On the other hand, in \mathcal{A}_2 the reference state could be either locally or globally stable.

Taking now the reference state in \mathcal{A}_3 as globally stable, we conclude from the foregoing discussion that it migrates slightly upon crossing the critical line C from \mathcal{A}_3 into \mathcal{A}_1 , whereas it jumps abruptly upon crossing the point C from \mathcal{A}_3 in \mathcal{A}_4 . Such a behavior is only compatible with the presence of a first-order transition line emanating from C within \mathcal{A}_2 and with the interpretation of the portion of the line C that separates \mathcal{A}_1 and \mathcal{A}_3 as a second-order transition line.

Thus, C is a tricritical point, because there two different transition lines meet: one is first order, the other second order. In Fig. 1, according to Griffiths' notation [18], first-order transitions are represented by a solid line, while second-order transitions are represented by a broken line.

In conclusion, the *tricritical manifold* is defined by Eqs. (24) and (26) and the conditions

$$\frac{\partial^2 \mathcal{F}}{\partial T'^2}(S_0(\beta, \lambda), 0, \beta, \lambda) = 0, \quad (32a)$$

$$\begin{aligned} & \frac{\partial^4 \mathcal{F}}{\partial T'^4}(S_0(\beta, \lambda), 0, \beta, \lambda) \frac{\partial^2 \mathcal{F}}{\partial S^2}(S_0(\beta, \lambda), 0, \beta, \lambda) \\ & - 3 \left(\frac{\partial^3 \mathcal{F}}{\partial T'^2 \partial S}(S_0(\beta, \lambda), 0, \beta, \lambda) \right)^2 > 0 \end{aligned} \quad (32b)$$

determine the portion of the critical line consisting of second-order transition points.

Finally, we note for later use that a better approximation for the equilibrium phase near the reference state can be obtained in the admissible set from Eqs. (20) and (21):

$$\delta S = \frac{F_1 F_3}{4F_2 F_4 - F_3^2 - 2F_1 F_6}, \quad (33)$$

$$T'^2 = \frac{(F_1 F_6 - 2F_2 F_4) F_1}{4F_2 F_4 - F_3^2 - 2F_1 F_6 F_2}. \quad (34)$$

These formulas are useful in sketching the bifurcating solution branches and in continuing them numerically. A similar improvement of the lowest approximation employed above can be obtained for both the determinant of the Hessian matrix and the energy difference along the bifurcating branches [19].

IV. TRICRITICAL POINTS

In this section we apply the criterion presented above to the free energy \mathcal{F} in Eq. (8) for $\gamma=0$ and $\lambda > 0$. We shall choose as reference state either of the equilibrium phases predicted by Maier-Saupe's theory, to which the theory for biaxial nematics in Sec. II reduces when $\gamma=\lambda=0$.

As is well known, according to Maier-Saupe's theory, the isotropic phase corresponding to $S=0$ is accompanied by another locally stable equilibrium phase as soon as $\beta > \beta^* \approx 6.73$. This is the oriented nematic phase, which is characterized by the largest positive root $S_+(\beta)$ of the equilibrium equation

$$\frac{\partial \mathcal{F}}{\partial S} = 0,$$

which for $\lambda=0$ becomes

$$\frac{2}{3}S + \frac{1}{3} + \frac{1}{2S\beta} - \frac{\exp(S\beta)}{\sqrt{\pi S\beta} \text{Erfi}(\sqrt{S\beta})} = 0, \quad (35)$$

where

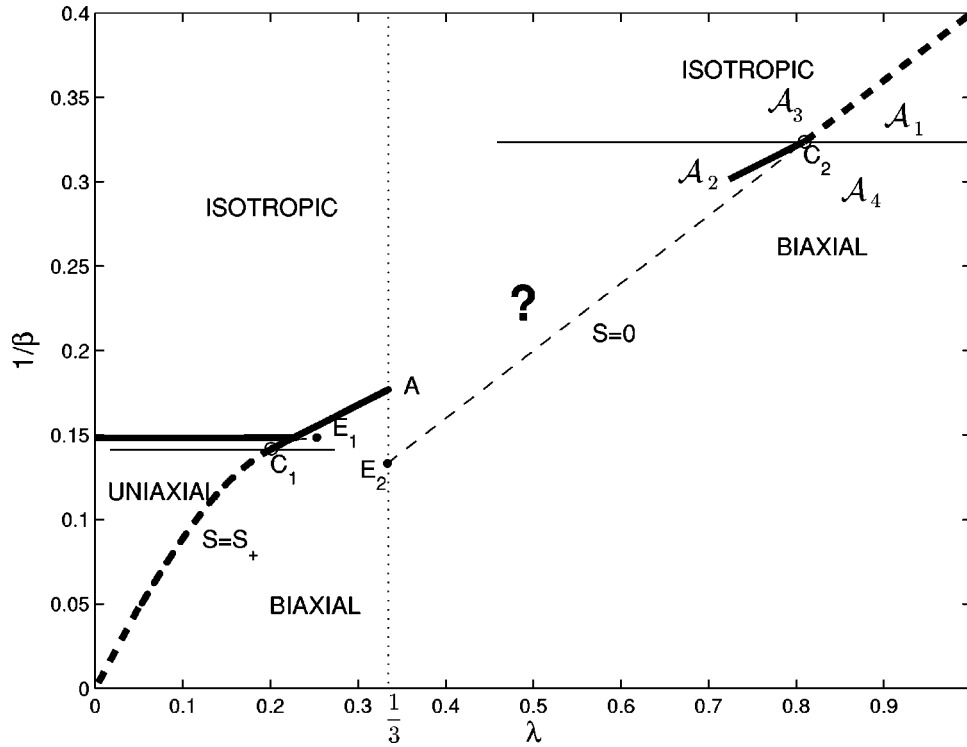


FIG. 2. Phase diagram in the plane $(\lambda, 1/\beta)$ associated with a model for biaxials [8]. The critical line relative to the uniaxial state $S=S_+$ and $T'=0$ starts from the origin and ends in E_1 : it is confined to the stable manifold $\beta > \beta^*$. The heavily dashed portion of this line, bounded by the line $\beta = \beta_t^{(1)}$, marks the second-order transition between uniaxial and biaxial phases. C_1 is the first tricritical point. The critical line relative to the isotropic phase $S=T'=0$ is confined to the stable manifold $\beta < 15/2$: it starts from the point E_2 and goes to infinity. It hosts the second tricritical point C_2 at $\beta = \beta_t^{(2)}$; the regions A_1 , A_2 , A_3 , and A_4 have the same meaning as in Sec. III. The heavy dashed line starting from C_2 represents second-order transitions between isotropic and biaxial phases. The heavy line represents first-order phase transitions computed for $0 < \lambda < 1/3$ [8]: a bifurcation analysis is needed to know how the points A and C_2 are to be joined.

$$\text{Erfi}(x) := \frac{2}{\sqrt{\pi}} \int_0^x e^{t^2} dt \quad \text{for all } x \in \mathbb{R}. \quad (36) \quad \Sigma_{T'} = 0 \quad (39)$$

For $\beta > \beta_c \approx 6.81$, the nematic phase has indeed lower free energy than the isotropic phase, which is still locally stable, and so the system undergoes a first-order phase transition. For $\beta > \beta_* = \frac{15}{2}$, the isotropic phase becomes locally unstable and another equilibrium ordered phase with a negative order parameter $S_-(\beta)$ arises; in the absence of any external field, this phase never attains the least energy, and so it fails to be globally stable. When $\lambda = 0$, the only phase transition undergone by the system occurs at $\beta = \beta_c$, where S condenses in S_+ .

Taking as reference state the uniaxial phase described by the pair $(S_+(\beta), 0)$, we compute the following eigenvalues of the Hessian matrix $[H_0]$:

$$\Sigma_S(\beta) = \frac{2}{3} \left[\frac{5}{2} + \frac{\beta}{3} (2S_+^2 - 2S_+ - 1) \right], \quad (37)$$

$$\Sigma_{T'}(\beta, \lambda) = \frac{1}{12} \lambda [24 + (3 - 10\beta - 14S_+\beta)\lambda], \quad (38)$$

where $\Sigma_S > 0$ for $\beta > \beta^* \approx 6.73$. The critical and singular lines are represented by the equations

and

$$\frac{\lambda^4}{27648S_+^2} [2025 + 180(-3 + 17S_+ + 3S_+^2)\beta + 12(3 - 184S_+ - 652S_+^2 + 74S_+^3)\beta^2 + 80S_+(3 + 97S_+ + 181S_+^2 + 7S_+^3)\beta^3 + 16S_+^2(-65 - 192S_+ + 3S_+^2 + 254S_+^3)\beta^4] = 0, \quad (40)$$

respectively (see also Appendix A). Thus, the tricritical points are identified as the common roots of Eqs. (39) and (40).

Figure 2 shows both critical and singular lines described by Eqs. (39) and (40) on the plane $(\lambda, 1/\beta)$. In particular, since the critical line is meaningful only when $\Sigma_S > 0$, the curve corresponding to Eq. (39) is restricted to the region where $\beta > \beta^*$, and so it ends at the point E_1 , where $\beta = \beta^*$. Moreover, since for $\lambda > 0$ the roots of Eq. (40) are independent of λ , the singular line has the equation $\beta = \beta_t$, where β_t is the root of the function of β within brackets in Eq. (40). By use of the asymptotic behavior of S_+ for $\beta \rightarrow \infty$,

$$S_+(\beta) \approx \frac{1}{2} \left(1 + \sqrt{1 - \frac{6}{\beta}} \right), \quad (41)$$

it is easily shown that there exists a single root $\beta_t^{(1)}$. The tricritical point C_1 in Fig. 2 has the following coordinates:

$$(\beta_t^{(1)}, \lambda_t^{(1)}) \approx (7.07, 0.20), \quad (42)$$

with $S_t = S_+(\beta_t^{(1)}) \approx 0.53$. It coincides with the point found in Ref. [8] by inspecting the numerical solutions of the equilibrium equations. By applying Eq. (32b), we conclude that the portion of the critical line that marks a second-order transition between uniaxial and biaxial phases is the one heavily dashed in Fig. 2. This figure also depicts the lines of first-order transitions computed for $0 < \lambda < \frac{1}{3}$ in Ref. [8].

A question that was not addressed in Ref. [8] is whether the transition between isotropic and biaxial phases can possibly become second order. To answer this question, we also study this model for $\lambda > \frac{1}{3}$ and we take the isotropic phase as reference state in our criterion. We compute both Σ_S and $\Sigma_{T'}$, for $S = T' = 0$:

$$\Sigma_S(\beta, \lambda) := \frac{\partial^2 \mathcal{F}}{\partial S^2}(0, 0) = \frac{1}{3} - \frac{2\beta}{45}, \quad (43)$$

$$\Sigma_{T'}(\beta, \lambda) := \frac{\partial^2 \mathcal{F}}{\partial T'^2}(0, 0) = \lambda - \frac{2\lambda^2\beta}{5}. \quad (44)$$

It follows from Eq. (43) that $\Sigma_S > 0$ for $\beta < \frac{15}{2}$ and that the critical line is represented by the equation

$$\frac{1}{\beta} = \frac{2\lambda}{5}. \quad (45)$$

The singular line is now (see also Appendix A)

$$\beta^3 \lambda^4 (34\beta - 105) = 0. \quad (46)$$

It is clear that Eqs. (45) and (46) have only the root

$$(\beta_t^{(2)}, \lambda_t^{(2)}) = \left(\frac{105}{34}, \frac{17}{21} \right), \quad (47)$$

which identifies a second tricritical point C_2 . By Eq. (32b), the heavy dashed line emanating in Fig. 2 from C_2 represents the locus of second-order transitions between isotropic and biaxial phases.

The criterion presented here can only predict the existence of this second tricritical point, where the phase transition between isotropic and biaxial phases becomes second order. It says nothing on how to complete the phase diagram in the plane $(\lambda, 1/\beta)$ for $\frac{1}{3} < \lambda < \lambda_t^{(2)}$: this requires a bifurcation analysis of the equilibrium phases, which will be undertaken elsewhere [19].

V. CONCLUSION

It was remarked in Ref. [8] that the model proposed there for biaxial nematics has a striking resemblance to McMillan's model for smectic A phases [20], in that it predicts a similar phase diagram with a tricritical point. The original motivation of our paper was to find a criterion to locate tricritical points for biaxial liquid crystal phases, sufficiently general to confirm the tricritical point already known and possibly to predict other such points still unknown.

The main outcome of our study was to predict the existence of another tricritical point in the phase diagram for biaxial nematics according to the model employed in Ref. [8], which should occur in a range of parameters not yet explored. A bifurcation analysis of the whole class of equilibrium phases predicted by the model in Ref. [8] is still needed to complete the phase diagram. This study, which just started, will be the object of a future paper [19].

Another question soon to be addressed concerns the second tricritical point we predict along the direct transition between the isotropic and biaxial phases: does it persist when the parameter γ is also switched on? It has long been known that for $\lambda=0$ the term proportional to γ in Straley's pair potential does not promote biaxial phases [21]. It remains to be seen whether increasing γ for $\lambda > \lambda_t^{(2)}$ would cause the reappearance of a uniaxial phase between the isotropic and biaxial ones. This would bound the extent of the direct uniaxial-to-biaxial transition, which is another distinctive feature of the model proposed in Ref. [8].

APPENDIX A: MATHEMATICAL DETAILS

In this appendix we list the coefficients of the expansion in Eq. (15) for the free energy \mathcal{F} that enter the definitions of both the critical and singular lines for the model studied here. We distinguish explicitly two cases: the one where $S = S_0 \neq 0$ and the one where $S = 0$. In the former case, repeated use of Eq. (35) is made.

1. $S = S_0$

$$F_1(S_0, \beta, \lambda) = \frac{1}{2} \Sigma_{T'}(\beta, \lambda) = \frac{1}{24} \lambda [24 + (3 - 10\beta - 14S_0\beta)\lambda],$$

$$F_2(S_0, \beta, \lambda) = \frac{[945 + 18\beta(8S_0^2 - 135S_0 - 7) + 12S_0\beta^2(26 + 287S_0 - 112S_0^2) + 8S_0^2\beta^3(392S_0^2 + 185S_0 - 1)]\lambda^4}{18432S_0^2},$$

$$F_3(S_0, \beta, \lambda) = \frac{[-45 + \beta(6 + 132S_0 - 12S_0^2) + 28S_0\beta^2(2S_0^2 - S_0 - 1)]\lambda^2}{144S_0},$$

$$F_4(S_0, \beta) = \frac{1}{2}\sum_S(\beta) = \frac{1}{18}[15 + (-2 - 2S_0 + 4S_0^2)\beta].$$

2. $S=0$

$$F_1(\beta, \lambda) = \frac{1}{2}\sum_{T'}(\beta, \lambda) = \lambda\left(1 - \frac{2\beta\lambda}{5}\right),$$

$$F_2(\beta, \lambda) = \frac{4\beta^3\lambda^4}{175},$$

$$F_3(\beta, \lambda) = -\frac{8\beta^2\lambda^2}{105},$$

$$F_4(\beta) = \frac{1}{2}\sum_S(\beta) = \frac{1}{3} - \frac{2\beta}{45}.$$

APPENDIX B: CRITERIA COMPARISON

In this appendix, more pedagogical in character, we briefly recall the definition of tricritical points and we compare the criterion presented here to locate them with those already known from the literature on critical phenomena.

In general, tricritical points occur whenever *three* coexisting fluid phases become simultaneously identical [14]. A tricritical point is thus different from both a critical point, where only two coexisting phases become identical, and a critical end point, where two phases become identical, in the presence of a third dissimilar phase. Ordered soft matter systems other than fluid mixtures can also exhibit tricritical points: there, three ordered phase become identical. Often two such phases are conjugated by a symmetry transformation: when this is the case, the tricritical points are referred to as being symmetric [14]. Symmetric tricritical points are common in liquid crystal phases, where the underlying molecular symmetry is more likely to induce them [20,22–24]. In Griffiths' terminology [18], a tricritical point is also a point on a phase diagram where a first-order transition becomes second order (the equivalence between these two definitions of a tricritical point is well explained, for example, in pp. 29–30 of Ref. [25]; Ref. [26] is another relevant general reference).

Within a simplified model describing the ordered phase of a system in terms of a single order parameter ψ , the free energy \mathcal{F} can be given the following Landau expansion:

$$\mathcal{F} = a_2\psi^2 + a_4\psi^4 + \psi^6 + o(\psi^6), \quad (\text{B1})$$

where only even powers of ψ are retained since ψ and $-\psi$ are thought of as corresponding to one and the same state. The coefficients a_2 and a_4 in Eq. (B1) depend on a set of physical

field variables, generally including the temperature. The coefficient of ψ^6 , which must be positive for thermodynamic stability, is set equal to unity, as its specific value is inessential [15]. In this simplified setting, the criterion for the existence of a tricritical point is given by the equations [14,15]

$$a_2 = a_4 = 0. \quad (\text{B2})$$

These equations have been extended to multicomponent fluid mixtures [27,28], though the reasoning was essentially left unchanged.

In liquid crystals, however, the occurrence of tricritical points is more likely related to ordered phases that need to be described by more than a single order parameter [8,20,22]. The criterion for tricritical points known in the liquid crystal literature [11–13] appears as an extension of the classical criterion (B2) based on the assumption that all order parameters can be seen as functions of a leading one, which is different from zero only in the ordered phase and which then makes all other order parameters differ from zero as well. Under this assumption, \mathcal{F} can again be given an effective form as in Eq. (B1), but with both a_2 and a_4 expressed in terms of the coefficients of the Landau expansion of \mathcal{F} thought of as a function of all independent order parameters.

Taking in our setting T' as the leading order parameter and denoting by f the function linking $\delta S := S - S_0$ to T' , so that $\delta S = f(T')$, we easily see that the path of equilibrium states in the vicinity of the reference state $(S_0, 0)$, where $\delta S = T' = 0$, is described by the equations

$$\frac{\partial(\Delta\mathcal{F})}{\partial T'}(f(T'), T') = 0, \quad \frac{\partial(\Delta\mathcal{F})}{\partial(\delta S)}(f(T'), T') = 0, \quad (\text{B3})$$

where $\Delta\mathcal{F}$ is defined as in Eq. (31). It follows from the second of Eqs. (B3) that

$$\frac{\partial^2(\Delta\mathcal{F})}{\partial(\delta S)\partial T'} + \frac{\partial^2(\Delta\mathcal{F})}{\partial(\delta S)^2}f' = 0, \quad (\text{B4})$$

where a prime denotes differentiation with respect to T' . Since $\Delta\mathcal{F}$ is symmetric in T' , also by Eq. (27), Eq. (B4) implies that f' vanishes at the reference state $(S_0, 0)$, whenever this lies on the critical line. Thus, evaluating both $(\Delta\mathcal{F})''$ and $(\Delta\mathcal{F})''''$ at the reference state, we find that there

$$(\Delta\mathcal{F})'' = \left(\frac{\partial^2\mathcal{F}}{\partial T'^2}\right)_{(S_0, 0)},$$

$$(\Delta\mathcal{F})'''' = \left(\frac{\partial^4 \mathcal{F}}{\partial T^4} \right)_{(S_0,0)} - \frac{3}{\left(\frac{\partial^2 \mathcal{F}}{\partial S^2} \right)_{(S_0,0)}} \times \left(\frac{\partial^3 \mathcal{F}}{\partial T^2 \partial S} \right)_{(S_0,0)}^2.$$

Requiring both $(\Delta\mathcal{F})''$ and $(\Delta\mathcal{F})''''$ to vanish, as prescribed by Griffiths' criterion, reproduces our Eqs. (24) and (26).

This shows that the existing criterion [11–13], which assumes the existence of a leading order parameter, reduces to ours, which does not require that assumption. Thus, strictly speaking, the criterion presented in this paper is potentially more general than that commonly employed in the liquid crystal literature. However, since the tricriticality criterion was here more a tool than a goal, we abstain from claiming to have contributed to the general theory of critical phenomena.

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