Bulk and surface biaxiality in nematic liquid crystals

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Nematic liquid crystals possess three different phases: isotropic, uniaxial, and biaxial. The ground state of most nematics is either isotropic or uniaxial, depending on the external temperature. Nevertheless, biaxial domains have been frequently identified, especially close to defects or external surfaces. In this paper we show that any spatially varying director pattern may be a source of biaxiality. We prove that biaxiality arises naturally whenever the symmetric tensor $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$ possesses two distinct nonzero eigenvalues. The eigenvalue difference may be used as a measure of the expected biaxiality. Furthermore, the corresponding eigenvectors indicate the directions in which the order tensor $\mathbf{Q}$ is induced to break the uniaxial symmetry about the director $\mathbf{n}$. We apply our general considerations to some examples. In particular we show that, when we enforce homeotropic anchoring on a curved surface, the order tensor becomes biaxial along the principal directions of the surface. The effect is triggered by the difference in surface principal curvatures.

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Nematic liquid crystals are aggregates of rodlike molecules. Early theories [1–3] used a single order parameter, the *director*, a unit vector pointing along the average microscopic molecular orientation. Most nematic phenomena fit well within the classical description. However, the transition from ordered to disordered states escapes the director theory. The classical microscopic description of defects and surface phenomena yields undesired results as well. The order-tensor theory put forward by de Gennes [4,5] focuses on the orientational probability distribution, and introduces the measures of the degree of orientation and biaxiality. Within this theory, a nematic liquid crystal possesses three different phases, which can be identified through their optical properties, since its Fresnel ellipsoid is closely related to the order tensor itself [6]. A *isotropic* liquid crystal is characterized by an isotropic order tensor, and optically behaves as an ordinary fluid. A *uniaxial* nematic possesses a unique optic axis. Its order tensor has two coincident eigenvalues. Finally, in a *biaxial* nematic the eigenvalues of the order tensor are all different, and the Fresnel ellipsoid possesses two optic axes.

Within the Landau-de Gennes theory, the ground state may be either isotropic or uniaxial, depending on the external temperature. However, biaxial domains have been predicted and observed, especially close to defects and external boundaries. Schopohl and Sluckin [7] analyzed in detail the biaxial core of a $+\frac{1}{2}$ nematic disclination. More recent studies show that a biaxial *cloud* surrounds most nematic defects [8], and both analytic [9,10] and numeric [11,12] asymptotical descriptions of biaxial defect cores have been derived. Other examples of defect-induced biaxiality involve integer-charged disclinations [13–15] and cylindrical inclusions [16]. The onset of surface biaxiality is closely related to the presence of a symmetry-breaking special direction, which coincides with the surface normal [17]. Indeed, biaxiality has been predicted close to both external boundaries [18,19] and internal isotropic-nematic interfaces [20,21].

In this paper we show that biaxiality effects are closely related to, but not exclusively confined to, the examples above. In fact, within any spatially varying director distribution, the director gradient itself breaks uniaxial symmetry about the director. We analyze in detail the structure of the elastic free energy density and come up to the result that, given the director distribution, it is possible to predict the onset of biaxiality, to determine the direction of the secondary optic axis, and to estimate the intensity of biaxiality effects. We then apply our general considerations to some specific examples, both within the bulk and close to an external boundary. We remark that we are not dealing with intrinsically biaxial nematic liquid crystals, that is systems in which the ground state itself becomes biaxial. Such systems, first observed by Yu and Saupe [22], deserve a different treatment [23,24], since in them uniaxial symmetry is broken already at a molecular level.

This paper is organized as follows. In Secs. I and II we quickly review the order-tensor theory and the free energy density we aim at minimizing. In Sec. III we derive and describe our main result, predicting a possible onset of biaxiality whenever the director is not uniform. In the following Secs. IV and V we apply the preceding results to some specific examples. In Sec. VI we collect and discuss our main results, while in the Appendices we collect the technical details of the proofs.

I. ORDER TENSOR

The orientation of a single nematic molecule may be represented by a unit vector $\mathbf{n}\in\mathbb{S}^2$, where $\mathbb{S}^2$ is the unit sphere. Microscopic disorder is taken into account by introducing a probability measure $f_x:\mathbb{S}^2\rightarrow\mathbb{R}^+$, such that $f_x(\mathbf{m})$ describes the probability that a molecule placed in x is oriented along $\mathbf{m}$. The probability measure f_x is even, since opposite orientations are physically equivalent.

Nematic optics is determined by the variance tensor $\mathbf{M}=\langle\mathbf{m}\otimes\mathbf{m}\rangle$, where the tensor product is defined in (A8) and the brackets denote averaging with respect to f_x. By definition, $\mathbf{M}$ is symmetric and semidefinite positive. Since, in addition, the trace of $\mathbf{M}$ is equal to 1, we define the traceless

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order tensor $\mathbf{Q}=\mathbf{M}-\frac{1}{3}\mathbf{I}$, where $\mathbf{I}$ is the identity.

We label the nematic as *isotropic* when all the eigenvalues of $\mathbf{Q}$ coincide, which implies $\mathbf{Q}_{\rm iso}=\mathbf{0}$. When at least two eigenvalues are equal, the nematic is called *uniaxial*. Simple algebraic manipulations allow one to write

$$\mathbf{Q}_{\rm uni}=s\left(\mathbf{n}\otimes\mathbf{n}-\frac{1}{3}\mathbf{I}\right). \tag{1}$$

The scalar parameter s is the *degree of orientation* [25], while the unit vector $\mathbf{n}$ is the *director*. The eigenvalues of $\mathbf{Q}_{\rm uni}$ are $\frac{2}{3}s$ (associated with $\mathbf{n}$) and $-\frac{1}{3}s$ (with a multiplicity of 2). The director is then the eigenvector associated with the different eigenvalue. Equivalently, $\mathbf{n}$ could be also identified as the eigenvector associated with the eigenvalue whose sign is different from the other two.

When the eigenvalues of the order tensor are all different, the nematic is labeled as *biaxial*. In this general case, we can use the above remark, and still identify the director as the eigenvector of $\mathbf{Q}$ whose eigenvalue has a different sign with respect to the other two. This definition may induce an artificial director discontinuity whenever the intermediate eigenvalue crosses 0. In turn, it yields an operative definition that works well when the order tensor is possibly biaxial, but however, close to being uniaxial. Once we have introduced the director, we again define the degree of orientation $s=\frac{3}{2}\lambda_{\rm n}$, where $\lambda_{\rm n}$ is the eigenvalue associated with $\mathbf{n}$. The other two eigenvalues $\lambda_\pm$ can be finally written in terms of the *degree of biaxiality* β: $\lambda_\pm=-\frac{1}{3}s\pm\beta$. As a result we obtain

$$\mathbf{Q}_{\rm bia}=s\left(\mathbf{n}\otimes\mathbf{n}-\frac{1}{3}\mathbf{I}\right)+\beta(\mathbf{e}_+\otimes\mathbf{e}_+-\mathbf{e}_-\otimes\mathbf{e}_-). \tag{2}$$

The sign of β is unessential, since it only involves an exchange between $\mathbf{e}_+$ and $\mathbf{e}_-$. The degree of biaxiality does always satisfy $|\beta|\leqslant\frac{1}{3}|s|$. Indeed, when $|\beta|=\frac{1}{3}|s|$ one of the eigenvalues vanishes, and greater biaxiality values would in fact announce an abrupt change in the director (and in the degree of orientation as well).

II. FREE ENERGY FUNCTIONAL

Equilibrium states of nematic liquid crystals are identified as extremals of the free-energy functional whose density, in the absence of external fields, comprises two terms

$$\Psi(\mathbf{Q},\nabla\mathbf{Q})=\Psi_{\rm el}(\mathbf{Q},\nabla\mathbf{Q})+\Psi_{\rm LdG}(\mathbf{Q}). \tag{3}$$

Though all of the calculations we report could be repeated in a more general framework, we will adopt the one-constant approximation for the elastic contribution $\Psi_{\rm el}$,

$$\Psi_{\rm el}(\mathbf{Q},\nabla\mathbf{Q})=\frac{K}{2}|\nabla\mathbf{Q}|^2, \tag{4}$$

where K is an average elastic constant.

The Landau-de Gennes potential $\Psi_{\rm LdG}$ is a temperature-dependent thermodynamic contribution that takes into account the material tendency to spontaneously arrange in ordered or disordered states:

$$\Psi_{\rm LdG}(\mathbf{Q})=A\,{\rm tr}\mathbf{Q}^2-B\,{\rm tr}\mathbf{Q}^3+C\,{\rm tr}\mathbf{Q}^4. \tag{5}$$

The material parameter C must be positive to keep the free-energy functional bounded from below. The potential (5) depends only on the eigenvalues of $\mathbf{Q}$, and penalizes biaxial states [26]. Insertion of (2) into (5) returns

$$\Psi_{\rm LdG}(s,\beta)=\frac{2}{9}(Cs^4-Bs^3+3As^2)+\frac{2}{9}(6Cs^2+9Bs+9A)\beta^2+2C\beta^4. \tag{6}$$

Let $\alpha=3A/(Cs_0^2)$. The absolute minimum of $\Psi_{\rm LdG}$ is located at the uniaxial configuration ($s_0>0,\beta=0$), provided

$$\alpha\in[-2,1]\ \text{and}\ B=\tfrac{2}{3}Cs_0(\alpha+2). \tag{7}$$

When looking for minimizers of the free energy functional, we take into account that the Landau-de Gennes contribution usually dominates the elastic one. This approximation holds as long as we do not get too close to a nematic defect. Indeed, experimental observations confirm that neither s nor β depart easily from their preferred values $(s_0,0)$.

We then envisage a two-step minimization. In the first step (s,β) are constrained to their optimal values. Minimization proceeds exactly as in Frank's director theory and yields an optimal distribution $\mathbf{n}(\mathbf{r})$. In the second step, we fix the director distribution and determine the perturbative corrections it induces in the optimal values of the scalar order parameters. As a result, we prove that nonuniform director configurations may induce a nonzero degree of biaxiality, and a reduction in the degree of orientation. As a by-product we determine how a nonzero director gradient breaks the local axial symmetry induced by the director, and which direction is chosen by most molecules (among those orthogonal to $\mathbf{n}$).

III. BULK BIAXIALITY

We collect in the present section our main result. In order to ease the reader we defer most of the technical proofs to the Appendices below. We assume that a specific director distribution $\mathbf{n}(\mathbf{r})$ has been determined by minimizing Frank's free-energy functional, constrained by suitable boundary conditions. The director distribution may also take into account the effects of any possible external field.

In Appendix A we prove the following decomposition for the director gradient:

$$\nabla\mathbf{n}=\lambda_2\mathbf{e}_2\otimes\mathbf{e}_2+\lambda_3\mathbf{e}_3\otimes\mathbf{e}_3+({\rm curl}\ \mathbf{n}\wedge\mathbf{n})\otimes\mathbf{n}+\tfrac{1}{2}(\mathbf{n}\cdot{\rm curl}\ \mathbf{n})\mathbf{W}(\mathbf{n}), \tag{8}$$

where $\mathbf{W}(\mathbf{n})$ denotes the skew tensor associated with $\mathbf{n}$ (see Appendix A). Furthermore, $\{\lambda_2,\lambda_3\}$, $\{\mathbf{e}_2,\mathbf{e}_3\}$ are, respectively, the eigenvalues and eigenvectors of the symmetric part of $\mathbf{G}=\nabla\mathbf{n}-(\nabla\mathbf{n})\mathbf{n}\otimes\mathbf{n}$, the third eigenvector of sym $\mathbf{G}=\frac{1}{2}(\mathbf{G}+\mathbf{G}^T)$ being $\mathbf{n}$, with null eigenvalue. We remark that

$${\rm div}\ \mathbf{n}={\rm tr}\ \nabla\ \mathbf{n}=\lambda_2+\lambda_3. \tag{9}$$

Let $\mathbf{S}$ be the symmetric tensor $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$. By virtue of (A1) the director $\mathbf{n}$ is an eigenvector of $\mathbf{S}$ (with null eigenvalue). In Appendix B we prove that the elastic free energy density may be given the following form:

$$\Psi_{\text{el}} = K\Big[\tfrac{1}{3}|\nabla s|^2 + |\nabla \beta|^2 + s^2|\nabla \mathbf{n}|^2 + \beta^2(|\nabla \mathbf{n}|^2 + 4|(\nabla \mathbf{e}_+)^T\mathbf{e}_-|^2) - 2s\beta(\mathbf{e}_+\cdot\mathbf{S}\mathbf{e}_+ - \mathbf{e}_-\cdot\mathbf{S}\mathbf{e}_-)\Big]. \tag{10}$$

Let us analyze in detail the different terms appearing in (10). The first two terms are trivial, since they simply penalize spatial variations of the scalar order parameters. They remind that, even in the presence of spatially varying preferred values $(s_{\text{opt}}(\mathbf{r}), \beta_{\text{opt}}(\mathbf{r}))$, the equilibrium distribution may not imitate the optimal values. The third term is proportional to $s^2|\nabla\mathbf{n}|^2$. This term has been already extensively studied [25,27]. Its net effect is a decrease in the degree of orientation in places where the director gradient is most rapidly varying. In particular, it strongly pushes the system toward the isotropic state $s=0$ when the director gradient diverges. The second-last term is proportional to β^2. Since it is positive definite, it simply enhances the character of $\beta=0$ as an optimal biaxiality value. Thus, were it not for the final term we will next consider, biaxiality would never arise naturally in a nematic liquid crystal.

The last term in (10) is linear in β. It shifts the optimal biaxiality value away from $\beta=0$. In order to minimize the complete free energy density it is worth to maximize the multiplying factor depending on $\mathbf{S}$. This condition determines the directions $\{\mathbf{e}_+, \mathbf{e}_-\}$ in which the order tensor $\mathbf{Q}$ is pushed to break uniaxial symmetry. Indeed, the term within brackets is maximized when $\{\mathbf{e}_+, \mathbf{e}_-\}$ coincide with the two eigenvectors of $\mathbf{S}$ that are orthogonal to $\mathbf{n}$. If we denote by μ_+, μ_- the correspondent eigenvalues, the linear term becomes simply proportional to $(\mu_+ - \mu_-)$. We thus arrive at the following result. *Consider the symmetric tensor* $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$. *It always possesses a null eigenvalue (with eigenvector* $\mathbf{n}$*). Whenever its other two eigenvalues do not coincide, biaxiality is naturally induced in the system, and the optimal eigendirections of* $\mathbf{Q}$ *coincide with those of* $\mathbf{S}$.

If we take into account expression (8) for $\nabla\mathbf{n}$, we can give the eigenvalue difference $(\mu_+ - \mu_-)$ the following expression [see (A7)]:

$$(\mu_+ - \mu_-)^2 = (c_2^2 - c_3^2 + \lambda_3^2 - \lambda_2^2)^2 + 4\Big[c_2c_3 + \tfrac{1}{2}c_n(\lambda_3 - \lambda_2)\Big]^2, \tag{11}$$

where curl $\mathbf{n} = c_{\mathbf{n}} + c_2\mathbf{e}_2 + c_3\mathbf{e}_3$, and λ_2, λ_3 are as in (8). In the following sections we will apply the above results to some practical situations, in order to better interpret their implications.

IV. SPLAY, BEND, AND TWIST BIAXIALITY

A. Planar fields

We begin by considering a quite common case, that is a situation in which the director is everywhere orthogonal to a fixed direction $\mathbf{e}_z$. When this is the case we can write

$$\mathbf{n}(\mathbf{r}) = \cos\theta(\mathbf{r})\mathbf{e}_x + \sin\theta(\mathbf{r})\mathbf{e}_y, \tag{12}$$

where the tilt angle θ may depend on all three coordinates. Easy manipulations allow to write $\nabla\mathbf{n} = \mathbf{n}_\perp \otimes \nabla\theta$, with $\mathbf{n}_\perp = -\sin\theta(\mathbf{r})\mathbf{e}_x + \cos\theta(\mathbf{r})\mathbf{e}_y$. Thus

$$\mathbf{S} = (\mathbf{n}_\perp \otimes \nabla\theta)(\nabla\theta \otimes \mathbf{n}_\perp) = |\nabla\theta|^2 \mathbf{n}_\perp \otimes \mathbf{n}_\perp. \tag{13}$$

The tensor $\mathbf{S}$ is symmetric as expected. Its eigenframe is $\{\mathbf{n}, \mathbf{n}_\perp, \mathbf{e}_z\}$, with eigenvalues $\{0, |\nabla\theta|^2, 0\}$. The relevant eigenvalue difference $(\mu_+ - \mu_-) = |\nabla\theta|^2$ induces spontaneous biaxiality whenever the tilt angle is not uniform. This result has a simple physical interpretation. Since the director does never lift from the $(\mathbf{e}_x, \mathbf{e}_y)$ plane, nematic molecules are naturally induced to avoid the direction $\mathbf{e}_z$. As a consequence, the order tensor breaks the uniaxial symmetry. It decreases the eigenvalue in the $\mathbf{e}_z$ direction, and consequently increases the planar eigenvalue associated with $\mathbf{n}_\perp$.

Among the many examples of nontrivial planar configurations we next analyze three particularly significant ones.

1. Pure splay

The splay field is defined as $\mathbf{n}(\mathbf{r}) = \mathbf{e}_r$, where $\mathbf{e}_r$ is the radial unit vector in cylindrical coordinates. If we complete an orthonormal basis by introducing the tangential and axial unit vectors $\mathbf{e}_\theta, \mathbf{e}_z$, standard calculations allow one to prove that

$$\nabla\mathbf{n} = \frac{1}{r}\mathbf{e}_\theta \otimes \mathbf{e}_\theta \quad \text{and} \quad \mathbf{S} = \frac{1}{r^2}\mathbf{e}_\theta \otimes \mathbf{e}_\theta. \tag{14}$$

Thus, $\mu_+ = r^{-2}$, $\mu_- = 0$, and the elastic free energy density is given by

$$\Psi_{\text{el}} = K\left(\frac{1}{3}|\nabla s|^2 + |\nabla\beta|^2 + \frac{(s-\beta)^2}{r^2}\right). \tag{15}$$

Biaxiality favors the tangential direction with respect to the axial direction. The r^{-2} factor implies that biaxiality (and the degree of orientation decrease as well) is expected to show close to the symmetry axis. Figures 3 and 5 of Ref. [13] exactly confirm this result.

2. Pure bend

We again consider the same cylindrical coordinate frame above, and analyze the bend field $\mathbf{n}(\mathbf{r}) = \mathbf{e}_\theta$. We obtain

$$\nabla\mathbf{n} = -\frac{1}{r}\mathbf{e}_r \otimes \mathbf{e}_\theta \quad \text{and} \quad \mathbf{S} = \frac{1}{r^2}\mathbf{e}_r \otimes \mathbf{e}_r. \tag{16}$$

Again, $\mu_+ = r^{-2}$, $\mu_- = 0$, and the elastic free energy density can be given exactly the same expression (15). Biaxiality now favors the radial direction, and again concentrates close to the (disclination) symmetry axis.

3. Pure twist

In Cartesian coordinates the twist field is defined as $\mathbf{n}(\mathbf{r}) = \cos kz\mathbf{e}_x + \sin kz\mathbf{e}_y$. If we again introduce the unit vector $\mathbf{n}_\perp(\mathbf{r}) = -\sin kz\mathbf{e}_x + \cos kz\mathbf{e}_y$, we obtain

$$\nabla\mathbf{n} = k\mathbf{n}_\perp \otimes \mathbf{e}_z \quad \text{and} \quad \mathbf{S} = k^2\mathbf{n}_\perp \otimes \mathbf{n}_\perp. \tag{17}$$

We now have $\mu_+ = k^2$, $\mu_- = 0$. Again, biaxiality favors $\mathbf{n}_\perp$, that is, the (x,y) plane, with respect to the transverse direction $\mathbf{e}_z$. The elastic free energy density still coincides with (15), with only a k^2 replacing the r^{-2} factor. However, this coincidence must not induce one to guess that Ψ_{el} does always depend on s and β only through the combination $(s-\beta)$, as we will evidence below.

B. Third dimension escape

We now consider a nontrivial three-dimensional example: the escape in the third dimension. This field was first determined by Cladis and Kléman [28] as an everywhere continuous director field able to fulfill homeotropic boundary conditions on a cylinder. Let $\mathbf{n}(\mathbf{r}) = \cos\phi(r)\mathbf{e}_r + \sin\phi(r)\mathbf{e}_z$ be the director field, and let $\mathbf{n}_\perp(\mathbf{r}) = -\sin\phi(\mathbf{r})\mathbf{e}_r + \cos\phi(r)\mathbf{e}_\mathbf{z}$. We obtain

$$\nabla\mathbf{n} = \frac{\cos\phi}{r}\mathbf{e}_\theta\otimes\mathbf{e}_\theta + \phi'\mathbf{n}_\perp\otimes\mathbf{e}_r \quad\text{and}\quad \mathbf{S} = \frac{\cos^2\phi}{r^2}\mathbf{e}_\theta\otimes\mathbf{e}_\theta + \phi'^2\mathbf{n}_\perp\otimes\mathbf{n}_\perp. \tag{18}$$

Expression (18) for $\mathbf{S}$ shows that, within the order tensor $\mathbf{Q}$, either $\mathbf{n}_\perp$ or $\mathbf{e}_\theta$ may be preferred, depending on whether ϕ'^2 is greater or smaller than $\cos^2\phi/r^2$. This result turns out to be particularly challenging, if we consider that in Cladis-Kléman's escape in the third dimension the tilt angle ϕ is given by

$$\phi(r) = \frac{\pi}{2} - 2\arctan\frac{r}{R}. \tag{19}$$

A simple calculation allows one to show that (19) implies $\phi'^2 = \cos^2\phi/r^2$. Thus, the third-dimension escape turns out to be one of the few spatially varying director fields which do not induce any biaxiality. The elastic free-energy density in Cladis-Kléman's third-dimension escape is given by

$$\Psi_{el} = K\left(\frac{1}{3}|\nabla s|^2 + |\nabla\beta|^2 + \frac{8R^2s^2}{(r^2+R^2)^2} + \frac{4(R^4+r^4)\beta^2}{r^2(r^2+R^2)^2}\right). \tag{20}$$

V. SURFACE BIAXIALITY

In this section we estimate the degree of biaxiality induced by an external surface on which strong anchoring is enforced. We consider separately the cases of homeotropic and planar anchoring. Differential calculus formula that turn out to be useful for both cases are collected in Appendix C.

A. Homeotropic anchoring

We first assume that the surface director is parallel to the unit normal ν to a given (smooth) surface Σ. We also assume that the director keeps its normal direction, at least in a thin surface slab. To be more precise, we parametrize bulk points through a coordinate set (u,v,ξ) such that

$$P(u,v,\xi) = P_\Sigma(u,v) + \xi\boldsymbol{\nu}(u,v), \tag{21}$$

where P_Σ is the projection of P onto Σ, ξ is the distance of P from the fixed surface, and $\boldsymbol{\nu}$ is the unit normal at P_Σ (see Fig. 1). If Σ if smooth, the coordinate set is well defined in a finite neighborhood of Σ. We assume that $\mathbf{n}(P(u,v,\xi)) = \mathbf{n}(P_\Sigma(u,v)) = \boldsymbol{\nu}(u,v)$. Then, $\nabla\mathbf{n}$ turns out to be closely related to the curvature tensor. It is symmetric and can be written [see (C2)]

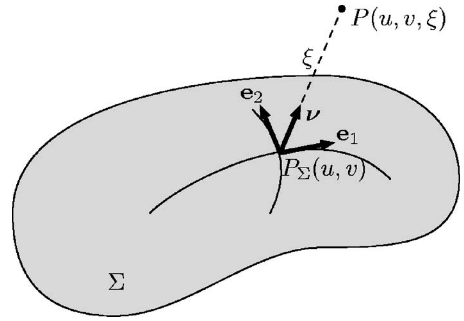

FIG. 1. Geometric setting for the surface parametrization introduced in the text.

$$\nabla\mathbf{n} = -\frac{\kappa_1}{1-\kappa_1\xi}\mathbf{e}_1\otimes\mathbf{e}_1 - \frac{\kappa_2}{1-\kappa_2\xi}\mathbf{e}_2\otimes\mathbf{e}_2, \tag{22}$$

where $\{\kappa_1,\kappa_2\}$ and $\{\mathbf{e}_1,\mathbf{e}_2\}$ denote, respectively, the principal curvatures and principal directions at P_Σ. From them we obtain curl $\mathbf{n}=0$, $\mathbf{G}=\nabla\mathbf{n}$, and

$$\mathbf{S} = \frac{\kappa_1^2}{(1-\kappa_1\xi)^2}\mathbf{e}_1\otimes\mathbf{e}_1 + \frac{\kappa_2^2}{(1-\kappa_2\xi)^2}\mathbf{e}_2\otimes\mathbf{e}_2. \tag{23}$$

Equation (23) shows that biaxiality arises naturally close to an external surface where homeotropic anchoring is enforced. This effect is triggered by the difference between the principal curvatures. More precisely, the tangent direction preferred by the order tensor is the one along which the surface curves more rapidly. Close to a symmetric saddle, where $\kappa_1=-\kappa_2$, the denominator of (23) induces biaxiality along the direction which is convex toward the side occupied by the liquid crystal.

B. Planar anchoring

When planar anchoring is enforced on a curved surface, it is natural to assume that the chosen direction coincides with one of the principal directions along Σ. We then keep the same notations as above, and assume $\mathbf{n}(P(u,v,\xi)) = \mathbf{n}(P_\Sigma(u,v)) = \mathbf{e}_1(u,v)$. When this is the case, by (C2) we obtain

$$\nabla\mathbf{n} = \frac{\kappa_1}{1-\kappa_1\xi}\boldsymbol{\nu}\otimes\mathbf{e}_1 \Rightarrow \text{curl }\mathbf{n} = -\frac{\kappa_1\mathbf{e}_2}{1-\kappa_1\xi},$$

$$\mathbf{G} = \mathbf{0}\ \text{and}\ \mathbf{S} = \frac{\kappa_1^2}{(1-\kappa_1\xi)^2}\boldsymbol{\nu}\otimes\boldsymbol{\nu}. \tag{24}$$

Thus, in the presence of planar anchoring, biaxiality arises whenever the curvature along the prescribed direction is different from zero. When this is the case, the biaxiality direction coincides with the unit normal.

VI. DISCUSSION

We have shown that any spatially varying director distribution may induce the onset in biaxial domains even in nematic liquid crystals whose ground state is strictly uniaxial. In particular, in Sec. III we have stressed the crucial role played by $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$. The tensor $\mathbf{S}$, which is symmetric and positive semidefinite by construction, possesses always a null eigenvalue, with eigenvector $\mathbf{n}$. Equation (10) shows that biaxiality arises naturally whenever the other two eigenvalues of $\mathbf{S}$ are different. Then, Eq. (11) shows that such eventuality is closely related to the vector curl $\mathbf{n}$ and the eigenvalues entering in the decomposition (8) of the director gradient.

In Sec. IV we have applied the considerations above to some model cases. As it could be easily predicted the pure splay, bend, and twist fields, being all planar, exhibit some degree of biaxiality which privileges the director plane over the orthogonal direction. A less trivial result is that there are spatially varying director configurations that do not induce biaxiality at all. Cladis-Kléman's escape in the third dimension yields a unexpected example of this phenomenon. Section V analyzes the onset of surface biaxiality both in the case of homeotropic and planar alignment. In the former case, biaxiality is ruled by the difference between the principal curvatures along the surface. In the latter, only one curvature counts, and more precisely the one along the prescribed direction in the tangent plane.

To conclude our analysis we want to give a numerical estimate of the magnitude of the biaxiality phenomena we are predicting. In all nontrivial cases, the free-energy density will contain a $O(\beta)$ term, which triggers the biaxiality onset. To obtain a rough estimate, we can neglect the $O(\beta^4)$ term in $\Psi_{\rm LdG}$, and the $O(\beta^2)$ term in $\Psi_{\rm el}$, both with respect to the dominant $O(\beta^2)$ term, appearing in $\Psi_{\rm LdG}$. When this is the case, the (local) preferred value of β may be obtained by minimizing the function

$$\begin{aligned} g(\beta) &= \frac{2}{9}(6Cs^2+9Bs+9A)\beta^2 - 2Ks\beta(\mu_+-\mu_-) \\ &\approx 2(2+\alpha)Cs_0^2\beta^2 - 2Ks_0\beta(\mu_+-\mu_-) \\ &= \frac{2Ks_0}{\xi_{\rm n}^2}(\beta^2-\xi_{\rm n}^2(\mu_+-\mu_-)\beta), \end{aligned} \quad (25)$$

where we have replaced $s\approx s_0$ and introduced the *nematic coherence length*

$$\xi_{\rm n}^2 = \frac{K}{Cs_0(2+\alpha)}. \quad (26)$$

The (local) optimal value of the degree of biaxiality is then

$$\beta_{\rm opt} \approx \tfrac{1}{2}\xi_{\rm n}^2(\mu_+-\mu_-). \quad (27)$$

Though $\beta_{\rm opt}$ may vary from point to point, we have to keep in mind that in general the equilibrium configuration will not coincide with $\beta_{\rm opt}$ because of the $|\nabla\beta|^2$ term, and the boundary conditions. To make an explicit example, let us consider a nematic cylindric capillary of radius R, with homeotropic conditions enforced at the surface. Then, the difference between the eigenvalues of $\mathbf{S}$ at the surface is R^{-2} and the surface biaxiality is of the order of $(\xi_{\rm n}/R)^2$. Since the nematic coherence length hardly exceeds the tenths of a μm, we obtain $\beta_{\rm opt}\lesssim 10^{-2}$ for a μm capillary. The scenario changes completely close to a nematic defect, where at least one of the eigenvalues of $\mathbf{S}$ diverges. Both the pure splay and the pure bend examples above yield $(\mu_+-\mu_-)=r^{-2}$, which implies $\beta_{\rm opt}\approx(\xi_{\rm n}/r)^2$. The biaxiality *cloud* cannot be neglected if we come too close to the defect.

APPENDIX A: DIRECTOR GRADIENT

In order to characterize the tensor $\nabla\mathbf{n}$ we begin by noticing that

$$(\nabla\mathbf{n})^T\mathbf{n} = \frac{1}{2}\nabla(\mathbf{n}\cdot\mathbf{n}) = \mathbf{0}, \quad (A1)$$

since $\mathbf{n}$ is a unit vector. Let sym $\mathbf{L}=\frac{1}{2}(\mathbf{L}+\mathbf{L}^T)$ and skw $\mathbf{L}=\frac{1}{2}(\mathbf{L}-\mathbf{L}^T)$ respectively denote the symmetric and the skew part of a tensor $\mathbf{L}$. Thus,

$$(\nabla\mathbf{n})\mathbf{n} = (\mathrm{sym}\,\nabla\,\mathbf{n}+\mathrm{skw}\,\nabla\,\mathbf{n})\mathbf{n} = \frac{1}{2}(\nabla\mathbf{n})\mathbf{n} + \frac{1}{2}\,\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n}, \quad (A2)$$

and $(\nabla\mathbf{n})\mathbf{n}=\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n}$. Let $\mathbf{G}=\nabla\mathbf{n}-(\nabla\mathbf{n})\mathbf{n}\otimes\mathbf{n}$. For any vector $\mathbf{v}$,

$$\begin{aligned} (\mathrm{skw}\,\mathbf{G})\mathbf{v} &= \big(\mathrm{skw}(\nabla\mathbf{n}) - \tfrac{1}{2}[(\nabla\mathbf{n})\mathbf{n}\otimes\mathbf{n} - \mathbf{n}\otimes(\nabla\mathbf{n})\mathbf{n}]\big)\mathbf{v} \\ &= \tfrac{1}{2}(\mathrm{curl}\,\mathbf{n} - \mathbf{n}\wedge(\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n}))\wedge\mathbf{v} \\ &= \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{n}\wedge\mathbf{v} = \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n})\mathbf{v}, \end{aligned} \quad (A3)$$

where $\mathbf{W}(\mathbf{n})$ denotes the skew tensor associated with $\mathbf{n}$, that is the tensor such that $\mathbf{W}(\mathbf{n})\mathbf{v}=\mathbf{n}\wedge\mathbf{v}$ for any $\mathbf{v}$. Thus,

$$\begin{aligned} \nabla\mathbf{n} &= \mathrm{sym}\,\mathbf{G} + \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n}) + (\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n})\otimes\mathbf{n} \\ &= \lambda_2\mathbf{e}_2\otimes\mathbf{e}_2 + \lambda_3\mathbf{e}_3\otimes\mathbf{e}_3 + \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n}) \\ &\quad + (\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n})\otimes\mathbf{n}, \end{aligned} \quad (A4)$$

where $\{\lambda_2,\lambda_3\}$ and $\{\mathbf{e}_2,\mathbf{e}_3\}$ are, respectively, the eigenvalues and eigenvectors of sym $\mathbf{G}$. The eigenvectors $\{\mathbf{e}_2,\mathbf{e}_3\}$ are orthogonal to $\mathbf{n}$, since (A3) implies

$$\begin{aligned} (\mathrm{sym}\,\mathbf{G})\mathbf{n} &= \mathbf{G}\mathbf{n} - (\mathrm{skw}\,\mathbf{G})\mathbf{n} \\ &= (\nabla\mathbf{n} - (\nabla\mathbf{n})\mathbf{n}\otimes\mathbf{n})\mathbf{n} - \frac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n})\mathbf{n} = \mathbf{0}. \end{aligned} \quad (A5)$$

Let us consider the symmetric tensor $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$. In view of the crucial role it plays in inducing biaxiality we now analyze it in more detail:

$$\begin{aligned} \mathbf{S} &= \big[\lambda_2\mathbf{e}_2\otimes\mathbf{e}_2 + \lambda_3\mathbf{e}_3\otimes\mathbf{e}_3 + \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n}) \\ &\quad + (\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n})\otimes\mathbf{n}\big]\big[\lambda_2\mathbf{e}_2\otimes\mathbf{e}_2 + \lambda_3\mathbf{e}_3\otimes\mathbf{e}_3 \\ &\quad - \tfrac{1}{2}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathbf{W}(\mathbf{n}) + \mathbf{n}\otimes(\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n})\big] \\ &= \lambda_2^2\mathbf{e}_2\otimes\mathbf{e}_2 + (\lambda_2-\lambda_3)(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})\mathrm{sym}(\mathbf{e}_2\otimes\mathbf{e}_3) + \lambda_3^2\mathbf{e}_3\otimes\mathbf{e}_3 \\ &\quad + \tfrac{1}{4}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2(\mathbf{I}-\mathbf{n}\otimes\mathbf{n}) + (\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n})\otimes(\mathrm{curl}\,\mathbf{n}\wedge\mathbf{n}). \end{aligned} \quad (A6)$$

Let $\{0,\mu_+,\mu_-\}$ be the eigenvalues of $\mathbf{S}$. The onset of biaxiality depends whether the latter two are equal or not. Let curl $\mathbf{n}=c_n\mathbf{n}+c_2\mathbf{e}_2+c_3\mathbf{e}_3$. From (A6) we obtain

$$(\mu_+-\mu_-)^2=(c_2^2-c_3^2+\lambda_3^2-\lambda_2^2)^2+4\left[c_2c_3+\tfrac{1}{2}c_n(\lambda_3-\lambda_2)\right]^2. \tag{A7}$$

We finally remind that, given two vectors $\mathbf{u},\mathbf{v}$, the tensor product $(\mathbf{u}\otimes\mathbf{v})$ is defined as the second-order tensor such that

$$(\mathbf{u}\otimes\mathbf{v})\mathbf{a}=(\mathbf{v}\cdot\mathbf{a})\mathbf{u}\text{ for any vector }\mathbf{a}. \tag{A8}$$

APPENDIX B: ORDER TENSOR GRADIENT

Let us differentiate Eq. (2). We obtain

$$\begin{aligned}\nabla\mathbf{Q}&=\left(\mathbf{n}\otimes\mathbf{n}-\tfrac{1}{3}\mathbf{I}\right)\otimes\nabla s+s(\nabla\mathbf{n}\odot\mathbf{n}+\mathbf{n}\otimes\nabla\mathbf{n})\\&\quad+(\mathbf{e}_+\otimes\mathbf{e}_+-\mathbf{e}_-\otimes\mathbf{e}_-)\otimes\nabla\beta\\&\quad+\beta(\nabla\mathbf{e}_+\odot\mathbf{e}_++\mathbf{e}_+\otimes\nabla\mathbf{e}_+-\nabla\mathbf{e}_-\odot\mathbf{e}_--\mathbf{e}_-\otimes\nabla\mathbf{e}_-),\end{aligned} \tag{B1}$$

where, given a second-order tensor $\mathbf{L}$ and a vector $\mathbf{u}$, $(\mathbf{L}\odot\mathbf{u})$ is defined as the third-order tensor such that

$$(\mathbf{L}\odot\mathbf{u})\mathbf{a}=\mathbf{L}\mathbf{a}\otimes\mathbf{u}\text{ for any vector }\mathbf{a}. \tag{B2}$$

When computing the square norm of $\nabla\mathbf{Q}$, we can make extensive use of the property (A1) and also take into account that

$$\mathbf{u}\cdot\mathbf{v}=0\Rightarrow(\nabla\mathbf{u})^T\mathbf{v}=-(\nabla\mathbf{v})^T\mathbf{u}. \tag{B3}$$

As a consequence, we obtain

$$\begin{aligned}|\nabla\mathbf{Q}|^2&=\tfrac{2}{3}|\nabla s|^2+2|\nabla\beta|^2+2s^2|\nabla\mathbf{n}|^2\\&\quad+2\beta^2(|\nabla\mathbf{e}_+|^2+|\nabla\mathbf{e}_-|^2+2|(\nabla\mathbf{e}_+)^T\mathbf{e}_-|^2)\\&\quad-4s\beta(|(\nabla\mathbf{n})^T\mathbf{e}_+|^2-|(\nabla\mathbf{n})^T\mathbf{e}_-|^2).\end{aligned} \tag{B4}$$

We can further simplify expression (B4) if we consider that

$$\begin{aligned}|\nabla\mathbf{e}_+|^2+|\nabla\mathbf{e}_-|^2&=|(\nabla\mathbf{e}_+)^T|^2+|(\nabla\mathbf{e}_-)^T|^2\\&=|(\nabla\mathbf{e}_+)^T\mathbf{n}|^2+|(\nabla\mathbf{e}_+)^T\mathbf{e}_-|^2+|(\nabla\mathbf{e}_-)^T\mathbf{n}|^2\\&\quad+|(\nabla\mathbf{e}_-)^T\mathbf{e}_+|^2\\&=|\nabla\mathbf{n}|^2+2|(\nabla\mathbf{e}_+)^T\mathbf{e}_-|^2\end{aligned} \tag{B5}$$

and that

$$|(\nabla\mathbf{n})^T\mathbf{u}|^2=(\nabla\mathbf{n})^T\mathbf{u}\cdot(\nabla\mathbf{n})^T\mathbf{u}=\mathbf{u}\cdot\mathbf{S}\mathbf{u}, \tag{B6}$$

provided we define $\mathbf{S}=(\nabla\mathbf{n})(\nabla\mathbf{n})^T$. By using (B5) and (B6) it is immediate to give (B4) the expression quoted in (10).

APPENDIX C: CURVATURE TENSOR

Let Σ be the smooth surface, which bounds the system we are interested in. Let $\boldsymbol{\nu}$ be the unit normal, everywhere pointing in the direction of the bulk. We parametrize points in the bulk through a coordinate set (u,v,ξ) such that

$$P(u,v,\xi)=P_\Sigma(u,v)+\xi\boldsymbol{\nu}(u,v), \tag{C1}$$

where P_Σ is the projection of P onto Σ, and ξ is the distance of P from the same surface. Such a coordinate set is well defined in a finite neighborhood of Σ.

Let us consider the vector field everywhere defined as $\boldsymbol{\tau}(P(u,v,\xi))=\boldsymbol{\nu}(P_\Sigma(u,v))$. The second-order tensor $\nabla\boldsymbol{\tau}$ is symmetric. It generalizes the *curvature tensor* $\nabla_\Sigma\boldsymbol{\nu}$, which is defined only on the tangent bundle of Σ. The eigenvectors of $\nabla\boldsymbol{\tau}$ coincide with those of the curvature tensor, and are thus the unit normal (with a null eigenvalue) and the (tangent) *principal directions* on Σ. If we introduce $\{\kappa_1,\kappa_2\}$, the *principal curvatures* on Σ, and their corresponding eigenvectors $\{\mathbf{e}_1,\mathbf{e}_2\}$, we have

$$\nabla\tau=-\frac{\kappa_1}{1-\kappa_1\xi}\mathbf{e}_1\otimes\mathbf{e}_1-\frac{\kappa_2}{1-\kappa_2\xi}\mathbf{e}_2\otimes\mathbf{e}_2,$$

$$\nabla\mathbf{e}_1=\frac{\kappa_1}{1-\kappa_1\xi}\boldsymbol{\nu}\otimes\mathbf{e}_1\text{ and }\nabla\mathbf{e}_2=\frac{\kappa_2}{1-\kappa_2\xi}\boldsymbol{\nu}\otimes\mathbf{e}_2. \tag{C2}$$

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