Extrinsic Curvature Effects on Nematic Shells

Gaetano Napoli
Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via per Monteroni, Edificio "Corpo O," 73100 Lecce, Italy

Luigi Vergori
Dipartimento di Matematica, Università del Salento, Strada Provinciale Lecce-Arnesano, 73100 Lecce, Italy
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When nematic liquid crystals are constrained to a curved surface, the geometry induces distortions in the molecular orientation. The mechanisms of the geometrical frustration involve the intrinsic as well as the extrinsic geometry of the underlying substrate. We show that the nematic elastic energy promotes the alignment of the flux lines of the nematic director towards geodesics and/or lines of curvature of the surface. As a consequence, the influence of the curvature can be tuned through the Frank elastic moduli. To illustrate this effect, we consider the simple case of nematics lying on a cylindrical shell. By combining the curvature effects with external magnetic fields, the molecular alignment can be reoriented or switched between two stable configurations. This enables the manipulation of nematic alignment for the design of new materials and technological devices.

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Nematic order on rigid or flexible curved substrates represents an intriguing field to explore, motivated by mathematical elegance and applications in soft condensed matter. Nematic liquid crystals consist of aggregates of rodlike molecules with orientational ordering [1], that is, described through a unit vector **n**, called the director. The existence of a locally preferred direction and the resulting anisotropic optical properties make liquid crystals very suitable for electro-optic devices. In several liquid crystals displays, the alignment of the molecular field is driven through an active matrix, allowing us to continuously apply voltage wave forms at every pixel. Other classes of liquid crystals devices exploit the bistability, i.e., the existence of two zero-field minimum energy orientations. Generally, such a behavior is achieved using chemical treatments of delimiting surfaces combined with external electric fields [2,3].

When nematics are confined on curved surfaces, the molecular field is influenced by both geometrical and topological constraints. In closed surfaces with spherelike topology, topological frustration unavoidably forces the presence of defects, i.e., points in which the director is undefined. This peculiarity provides a promising way to design supramolecular atoms with controllable valence [4]. Different defect structures have been observed in colloids coated with thin nematic films [5,6]. Furthermore, anisotropic ordering on surfaces with bending elasticity is common in biological membranes, where the competition with the membrane elasticity plays a prominent role in the growth [7] and morphology [8,9] of these systems. Finally, it should be mentioned that the study of superfluid helium on curved corrugated surfaces shares the same mathematical formalism with two-dimensional nematics [10].

In this Letter, we focus on the influence of the extrinsic geometry of a substrate on the alignment of nematics coating it. Powers and Nelson [11], for nematic flexible membranes, and Santangelo *et al.* [12], for columnar phases, have already considered director–substrate coupling introducing *ad hoc* terms in the free energy. A similar approach has been developed by Biscari and Terentjev [13] in the framework of the order-tensor theory. Here, we show that the influence of the extrinsic geometry is a direct consequence of the adaptation of the Frank continuum theory to surface director fields. Consequently, the alignment of the molecular field on a cylindrical surface can have one or two stable configurations, depending on the ratio between the twist and the bend elastic constants. External magnetic fields can be applied to drive the director orientation or to switch it between two locally stable states.

It is well-known that the Frank free energy penalizes nonuniform nematic configurations by associating a cost to any spatial derivative of **n**. In earlier models of two-dimensional nematic order [14–18], the director energy is formulated by using the covariant derivative of **n**. Thus, the extrinsic geometry of the substrate is automatically ruled out from the alignment mechanisms. However, the derivative of a vector field lying on a surface S possesses a tangent component, which is its covariant derivative, and a normal component that depends on the second fundamental form of S. When the latter is taken into account in the Frank potential, it produces a coupling between the director field and the curvature principal directions of S.

We start from ordinary nematics, where the energy due to the distortion of the molecular field is given by the celebrated Frank formula

$$W_{\rm nem} = \frac{1}{2}\int_V [K_1(\mathrm{div}\mathbf{n})^2 + K_2(\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2 + K_3|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2]dv, \tag{1}$$

where K_1, K_2, and K_3 are positive constants, whereas V represents the spatial domain that the nematic occupies. Pictures of the distortions corresponding to each energy term (the splay, twist, and bend energies, respectively) are given in all books on the fundamentals of liquid crystals theory.

When the director is regarded as a surface field, it is customary to assume that the twist term vanishes [6,19,20]. On the contrary, we find that generally, the twist energy does not vanish. An example is given by a tangential unit vector field $\mathbf{n}$ forming a constant angle (different from 0 and $\frac{\pi}{2}$) with the generatrices of a cylindrical surface. Indeed, as we will see below, the twist term, together with part of the bend energy, is responsible for the coupling between the director field and the substrate geometry.

In order to deal with surface free energies, we have recently explored the possibility of deriving a two-dimensional model as a limiting case of Eq. (1) [21]. Thus, we have considered that the nematic fills a thin region of thickness h around a regular surface S. With the assumptions (i) $\mathbf{n}$ aligns parallel to the surface S, (ii) $\mathbf{n}$ does not change in the thickness, and (iii) h is much smaller than the minimal radius of curvature of S, Eq. (1) reduces to

$$W^S_{\rm nem} = \frac{1}{2}\int_S [k_1(\mathrm{div}_s\mathbf{n})^2 + k_2(\mathbf{n}\cdot\mathrm{curl}_s\mathbf{n})^2 + k_3|\mathbf{n}\times\mathrm{curl}_s\mathbf{n}|^2]da, \tag{2}$$

where $k_i = hK_i$. The differential operator div_s and curl_s denote the surface divergence and the surface curl, respectively. Let $\boldsymbol{\nu}$ represent the normal to the surface and $\mathbf{t} = \boldsymbol{\nu}\times\mathbf{n}$ the conormal vector of $\mathbf{n}$ (Fig. 1). Thus, $\mathrm{div}_s\mathbf{n} = \kappa_{\mathbf{t}}$, whereas in the Darboux basis $\{\mathbf{n}, \mathbf{t}, \boldsymbol{\nu}\}$ we have $\mathrm{curl}_s\mathbf{n} = -\tau_{\mathbf{n}}\mathbf{n} - c_{\mathbf{n}}\mathbf{t} + \kappa_{\mathbf{n}}\boldsymbol{\nu}$. Here, we have introduced the geodesic curvatures of the flux lines of $\mathbf{t}$ and $\mathbf{n}$

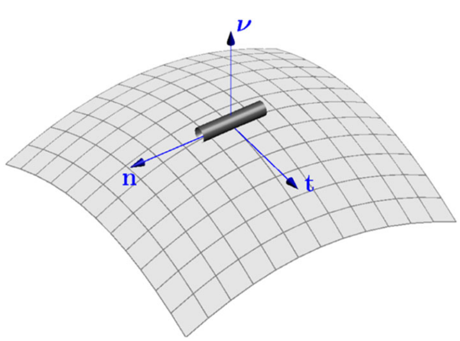

FIG. 1 (color online). Representation of the Darboux frame $\{\mathbf{n}, \mathbf{t}, \boldsymbol{\nu}\}$. At each point of the surface S, the unit vector $\mathbf{n}$ points along the optical axis. The unit vector $\mathbf{t}$, orthogonal to $\mathbf{n}$, lies on S. $\boldsymbol{\nu}$ is the normal to the shell.

denoted by $\kappa_{\mathbf{t}}$ and $\kappa_{\mathbf{n}}$, respectively, the normal curvature $c_{\mathbf{n}}$, and the geodesic torsion $\tau_{\mathbf{n}}$. We refer the reader to the book of do Carmo [22] for a more comprehensive treatise of the geometry of surfaces.

Consequently, Eq. (2) can be recast in the form

$$W^S_{\rm nem} = \frac{1}{2}\int_S [k_1\kappa_{\mathbf{t}}^2 + k_2\tau_{\mathbf{n}}^2 + k_3(\kappa_{\mathbf{n}}^2 + c_{\mathbf{n}}^2)]da \tag{3}$$

that lends itself well to an elegant and intuitive geometrical interpretation. From the geometry of surfaces we know that geodesic and torsion curvatures of a curve lying on a surface measure the deviance of the curve from following a geodesic or a line of curvature, respectively. Thus, from Eq. (3), we can recognize that the splay term tends to put the flux lines of $\mathbf{t}$ along geodesics of S as well as the part of the bend energy proportional to $\kappa_{\mathbf{n}}^2$ tries to put $\mathbf{n}$ along geodesics of S. In a similar way, the twist energy favors the alignment of the flux lines $\mathbf{n}$ with lines of curvature of S. Finally, the term proportional to $c_{\mathbf{n}}^2$ is minimized when $\mathbf{n}$ aligns with the principal direction of minimal curvature (in modulus).

To emphasize the difference with the models accepted in the literature, we write the simplest form of classical surface free energy

$$W^S_{\rm Class} = \frac{k}{2}\int_S D^\alpha n_\beta D_\alpha n^\beta da = \frac{k}{2}\int_S (\kappa_{\mathbf{t}}^2 + \kappa_{\mathbf{n}}^2)da, \tag{4}$$

where k is a positive constant, and D denotes the covariant derivative. We compare (4) with a *one constant approximation* version of (3)

$$W^S_{\rm nem} = \frac{k}{2}\int_S |\nabla_s\mathbf{n}|^2 da = \frac{k}{2}\int_S (\kappa_{\mathbf{t}}^2 + \tau_{\mathbf{n}}^2 + \kappa_{\mathbf{n}}^2 + c_{\mathbf{n}}^2)da.$$

Thus, in the classic energy Eq. (4) the twist energy, as well as the term proportional to $c_{\mathbf{n}}^2$, are missing. This mismatch can be explained by observing that the derivative of a vector $\mathbf{n}$ tangent to S along a direction $\mathbf{u}$ of the surface, namely, the surface gradient of $\mathbf{n}$ composed with $\mathbf{u}$, can be written as $(\nabla_s\mathbf{n})\mathbf{u} = D_{\mathbf{u}}\mathbf{n} + (\mathbf{n}\cdot\mathbf{L}\mathbf{u})\boldsymbol{\nu}$, where $\mathbf{L}$ denotes the extrinsic curvature tensor. On the other hand, the components of $\mathbf{L}$ in the Darboux frame are $L_{nn} = c_{\mathbf{n}}$, $L_{tt} = c_{\mathbf{t}}$, and $L_{nt} = L_{tn} = -\tau_{\mathbf{n}}$. Thus, the *extrinsic curvature* influences the free energy. However, apart from the trivial case of a flat surface, only for spherical surfaces is the literature model justified, forasmuch $\tau_{\mathbf{n}} = 0$ and $c_{\mathbf{n}}$ is a constant [6,16,23]. The twist term can be also neglected whenever one takes $\mathbf{n}$ along meridians or parallels of an axisymmetric surface [19].

Another interpretation of this result can be done within the covariant geometry formalism (see Appendix A of Ref. [24]). When considering nematic order on a shell, one starts by changing the three-dimensional flat space coordinates to Gaussian normal coordinates where two directions are the local coordinates on the shell and the third coordinate is perpendicular to it. The missing terms

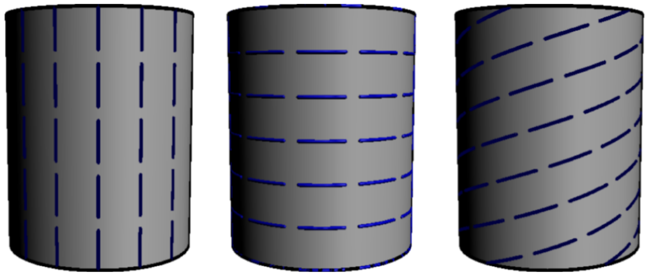

FIG. 2 (color online). Schematic representation of the solutions α_g, α_c, and α_{h_+}. The flux lines of **n** align along generatrices, circles, and helices of the cylinder, respectively.

arise because some of the Christoffel symbols in the thickness direction do not vanish. In particular, $\Gamma_{3ij} = L_{ij}$ and, therefore, derivatives along the perpendicular direction become covariant derivatives. This happens even if, like in our case, there is no explicit functional dependence of the director on the thickness direction.

However, this scenario can be further complicated by the presence of topological defects. In such a case additional terms must be added to describe the strength of the source or vortex at the singular points. For the sake of simplicity, hereinafter we discuss the case of a cylindrical shell, where the Poincaré-Hopf theorem ensures that no singular points are induced by the topology.

We consider a cylindrical surface of radius r and height L. This case provides an easy example where geodesics (generatrices, circles, and helices) and curvature lines (generatrices and circles) are immediately recognizable. Let us introduce a set of cylindrical coordinates (φ, z) as a set of local coordinates. Thus, $\mathbf{e}_\varphi$ and $\mathbf{e}_z$ will be unit vectors pointing in the radial and azimuthal directions, respectively. We denote with $\alpha(\varphi, z)$ the angle between the director and the parallel circles, and hence, the director is represented by $\mathbf{n} = \cos\alpha\mathbf{e}_\varphi + \sin\alpha\mathbf{e}_z$. Consequently, the total surface free energy becomes

$$W_{\text{nem}}^{\text{Cyl}} = \int_0^L dz \int_0^{2\pi} r d\varphi \bigg[\frac{k_2}{4r^2} \sin^2 2\alpha + \frac{k_3}{r^2} \cos^4 \alpha + k_1 (\mathbf{t} \cdot \nabla_s \alpha)^2 + k_3 (\mathbf{n} \cdot \nabla_s \alpha)^2 \bigg], \tag{5}$$

where $\nabla_s \alpha = r^{-1}(\partial_\varphi \alpha)\mathbf{e}_\varphi + (\partial_z \alpha)\mathbf{e}_z$.

We look for constant solutions for the equilibrium equation associated with Eq. (5). Uniform alignments along generatrices $\alpha_g = \frac{\pi}{2}$ and circles $\alpha_c = 0$ of the surface are always equilibrium configurations. Furthermore, whenever $k_2 > 2k_3$, it is found $\alpha_{h_\pm} = \pm \frac{1}{2} \arccos \frac{k_3}{k_2 - k_3}$; i.e., flux lines of **n** align along cylindrical helices (Fig. 2). By a direct inspection of the second variation of Eq. (5), we deduce (i) α_g is the absolute minimum of the free energy, (ii) α_c is locally stable whenever $k_2 > 2k_3$ and unstable whenever $0 \le k_2 \le 2k_3$, and (iii) $\alpha_{h_\pm}$ are always unstable.

We remark that in the literature models the first two terms in the integrand of Eq. (5) do not appear. As a consequence, any homogeneous (α = constant) configurations should be an equilibrium configuration with vanishing elastic energy. This clearly goes against physics intuition; indeed, whenever $\alpha \neq \frac{\pi}{2}$ the director aligns along helices or circles that are curves that bend in the space and, hence, they possess nonvanishing twist and bend energy.

We now study the influence of an external magnetic field on the stability of the solutions. In the presence of an external magnetic field **H**, the additional energy term

$$W_{\text{in}}^S = -\frac{\chi_a}{2} \int_S (\mathbf{n} \cdot \mathbf{H})^2 da, \tag{6}$$

describing the field–matter interaction, should be considered. It expresses the tendency of **n** to align parallel or orthogonal to **H** depending on the sign of the diamagnetic anisotropy χ_a. In the sequel, we assume $\chi_a > 0$. We consider an azimuthal field $\mathbf{H} = H\mathbf{e}_\varphi$, where the strength H is assumed to be constant. According to Ampere's law, such a field can be produced by a conducting wire situated along the cylinder axis. Thus, in the presence of an azimuthal magnetic field, the constant solutions satisfy the equation

$$\sin 2\alpha[(\lambda - 1)\cos 2\alpha - 1 + b^2] = 0, \tag{7}$$

where $\lambda = k_2/k_3$ denotes the nematic elastic anisotropy and $b = Hr\sqrt{\chi_a/k_3}$ represents the reduced magnetic field strength. Equation (7) admits always the trivial solutions α_g and α_c, whereas the solutions

$$\alpha_{h_\pm} = \pm \frac{1}{2} \arccos \frac{1 - b^2}{\lambda - 1}$$

are admitted provided that $\lambda < 1$ and $\lambda < b^2 < 2 - \lambda$ or $\lambda > 1$ and $2 - \lambda < b^2 < \lambda$. Hereinafter, we report different stability behavior depending on values of the parameter λ. The latter changes for different nematics, and it is temperature-dependent [25,26].

Whenever $\lambda < 1$, the stability analysis of the solutions predicts the existence of two critical thresholds

$$b'_{\text{cr}} = \sqrt{\lambda}, \qquad b''_{\text{cr}} = \sqrt{2 - \lambda}. \tag{8}$$

The director aligns along the cylinder generatrices unless the reduced applied field does not exceed b'_{cr}. When $b'_{\text{cr}} < b < b''_{\text{cr}}$, the sole stable solutions are $\alpha_{h_\pm}$. Above b''_{cr} the nematic director aligns along the circles of the surface. The change of alignment occurs smoothly as the field approaches the threshold values. The bifurcation diagram reported on the top of Fig. 3 mimes the behavior of the splay Freederickzs transition of a nematic cell with weak planar anchoring boundary conditions.

Within the one-constant approximation ($\lambda = 1$), only the solutions α_g and α_c are admitted. The thresholds b'_{cr} and b''_{cr} become equal to 1 and the phase transition between α_g and α_c becomes of the first order. Thus, at the critical

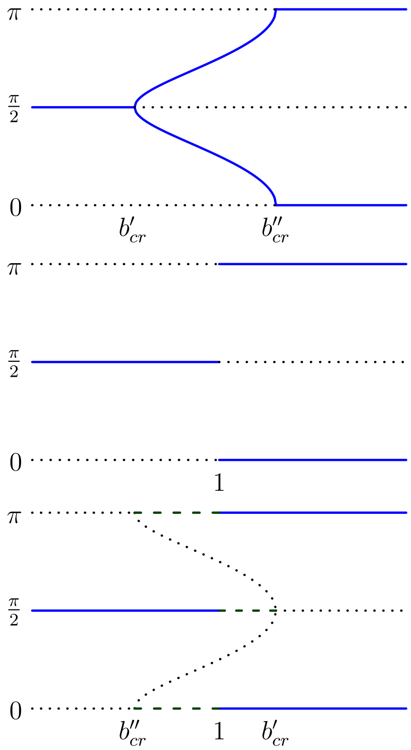

FIG. 3 (color online). Bifurcation diagram, α versus the reduced magnetic field b, for $0 \leq \lambda < 1$ (top), $\lambda = 1$ (middle), $1 < \lambda \leq 2$ bottom. The continuous, dashed, and dotted lines represent stable, metastable, and unstable configurations, respectively.

field, the director alignment abruptly switches between the two allowed states.

In the case $1 < \lambda \leq 2$, the nontrivial solutions $\alpha_{h_\pm}$ are unstable. The solutions α_g and α_c are unstable for $b \geq b'_{\mathrm{cr}}$ and $0 \leq b \leq b''_{\mathrm{cr}}$, respectively. In the range $b''_{\mathrm{cr}} < b < b'_{\mathrm{cr}}$, both the solutions are locally stable. The complete bifurcation diagram is sketched on the bottom of Fig. 3. Contrarily to the two previous cases, here the phenomenon is not reversible. In fact, starting from the fundamental configuration α_g and increasing the field strength, α_g switches to α_c when b exceeds b'_{cr}. By lowering the applied field, α_c switches to α_g at the critical threshold b''_{cr}.

Finally, we discuss the case $\lambda > 2$. This case differs from the previous, since in absence of any external field both the solutions α_g and α_c are minima. This suggests a potential way to design a bistable optical device, provided that a mechanism to switch between the two minima can be implemented. To achieve this aim, we can exploit two magnetic fields, one azimuthal as before and the other uniform in the $\mathbf{e}_z$ direction. In fact, α_g becomes unstable whenever b overcomes the critical field b'_{cr}. The total energy at the critical threshold b'_{cr}, represented by the dashed line in Fig. 4, shows how the azimuthal magnetic field destabilizes the configuration α_g. Once b'_{cr} has been exceeded, the external field can be relaxed, leaving the

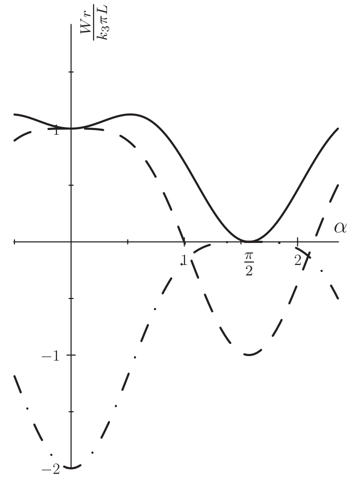

FIG. 4. Total energy as a function of the angle α, with zero field (continuous line), at the critical azimuthal threshold (dashed line) and at the critical axial threshold (dash-dotted line).

system in the local minima α_c. To perform the reverse path, we consider the uniform magnetic field $\mathbf{H}_z = H_z \mathbf{e}_z$. This field tends to rotate the molecules in the direction of the generatrices, and therefore, it destabilizes the solution α_c. More precisely, by setting $\bar{b} = H_z r \sqrt{\chi_a / k_3}$, α_c becomes unstable whenever $\bar{b} \geq \bar{b}_{\mathrm{cr}} = \sqrt{\lambda - 2}$. Coherently, the energy at the critical threshold $\bar{b}_{\mathrm{cr}}$ exhibits a unique minimum placed in $\alpha = \frac{\pi}{2}$.

To summarize, there are not physical or geometrical reasons to discard *a priori* the effects of the extrinsic curvature in two-dimensional curved nematics. Indeed, the classic Frank theory, when applied to surface fields, implies that twist and bend energies are responsible for the coupling between the directory and the curvature of the substrate. An application of our model to nematics lying on a cylindrical substrate demonstrates that curvature influences the stability of the molecular alignment. When this effect is combined with effects due to an applied magnetic field, it produces a miscellaneous collection of alignment properties potentially useful in the design of new technological optical devices. The alignment mechanism can be triggered with moderate magnetic fields. For instance, by taking $r \sim 10\ \mu\mathrm{m}$ and by considering values for MBBA near 25 °C (see page 330 of Ref. [27]), we obtain a critical magnetic field on the order of 10^4 oersted.

Another suitable setting allowing us to validate our approach follows. We consider a nematic with strong planar anchoring boundary conditions, $\alpha(0, \varphi) = \alpha(L, \varphi) = 0$. Whenever $k_2 < 2k_3$, the configuration $\alpha = 0$ is stable unless L does not exceed the critical value $L_{\mathrm{cr}} = \pi r \sqrt{k_1/(2k_3 - k_2)}$. In other words, the competitive effects between the curvature, which prefers the configuration $\alpha = \pi/2$, and the anchoring, which tries to restore the configuration $\alpha = 0$, induce a sort of Fréedericksz transition in the alignment. In the regime of *slim cylinder*

$L \gg r$, a thick central zone where the director aligns along the cylinder axis and two narrow regions close to the boundaries where the solution changes rapidly to satisfy the boundary conditions should be observed. On the other hand, the classical model predicts that the unique admitted solution is $\alpha = 0$.

We believe that our study will provide a novel paradigmatic description of two-dimensional systems with nematic ordering. The examples we have analyzed suggest possible experiments to be carried out to effectively test our model, which is in significant disagreement with the models commonly accepted. However, we are confident that this result may be important for future studies of nematic alignments in other geometry and topologies, location control of topological defects, nematic-mediated interaction on substrates, and influence of nematic ordering in morphology and growth of living membranes.

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