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Local Distortion Energy and Coarse-Grained Elasticity of the Twist-Bend Nematic Phase†

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The recently discovered twist-bend nematic phase of achiral bent-shaped molecules, N_{TB}, has doubly degenerate ground-state with periodically modulated heliconical structure and unusual distortion elasticity, the theoretical description o which is still debated. We show that the N_{TB} phase has the same macroscopic symmetry as another periodic mesophase, the chiral smectic-A, SmA*. Based on this N_{TB}/SmA* analogy, we develop a coarse-grained elastic model for the N_{TB} phase Adopting one of the existing microscopic N_{TB} elastic models, we calculate the coarse-grained elastic constants, coherence and penetration lengths in terms of a few Frank-like nematic elastic coefficients that can be measured in macroscop experiments. The same coarse-grained approach, applied to different local elastic models, may provide an efficie experimental test of their validity. We show that the anisotropy of the N_{TB} coarse-grained elasticity is opposite to that of the SmA*, leading probably to different configurations of some of the defects of the "layered" N_{TB} structure. Moreover, we argue that the intrinsic chiral frustration of the N_{TB} phase may be resolved by penetration of the twist field in the bul through a network of screw dislocations of the N_{TB} pseudo-layers, resulting in a twist-bend analogue of the twist grain boundary phase TGB_A.

Introduction

The nematic phase, N, is the most symmetric liquid crystal (LC) phase, exhibiting only orientational long-range order. Most often, it is formed by rod-like molecules, approximately aligned along the nematic director **n**. In the ground-state, **n** is uniform and its distortion costs some elastic energy. However, chiral molecules form a cholesteric (chiral nematic, N*) phase, with spontaneously twisted director and helical structure. The smectic phases present in addition positional long-range order - they have layered structures and different elastic properties.

Less symmetric molecules also form LC phases. Smectic and nematic phases of bent-shaped molecules, showing chiral symmetry breaking [1, 2] and giant flexoelectricity [3], have attracted much attention. Recently, a phase transition from the standard N phase to a distinct nematic, N_X, has been reported [4-9] for achiral bent-shape dimers. A detailed study by Cestari *et al.* [9] provided strong evidence that the N_X phase of the dimer CB7CB is a twist-bend nematic, N_{TB}: the molecules are arranged on a conical helix, with short pitch *p* and doubly degenerate chirality. This N_{TB} structure was rapidly confirmed experimentally for CB7CB and other bent-shape compounds [10-13].

Theoretically predicted long ago, the N_{TB} phase may arise from different physical mechanisms: transverse nematic ferroelectricity [14]; condensation of a polar-order wave [15, 16]; elastic instability due to spontaneous bend distortion [17]. Recent models treated also the elasticity [18-22] and the response to external fields [10, 23] of the N_{TB} phase, which is very important for both basic research and technological applications. In first approximation, the N_{TB} elasticity can be considered differently according to the length-scale. At short scale Λ, $\Lambda < p$, the elastic response is a function of the local deviation from the heliconical equilibrium N_{TB} structure. This local ("fine-grained") elasticity should be similar to the usual nemat elasticity, adapted[21] to the doubly degenerate N_{TB} structure (there is only one ground state in N and N* phases). The models proposed for this local elasticity [17-22] still await an indisputable experimental verification.

At large scale, $\Lambda >> p$, the N_{TB} elastic behaviour should be similar [10, 23, 24] to other periodic LC phases, like cholesterics and smectics. This large-scale elasticity, which is better described in terms of compression and curvature of the N_{TB} "pseudo-layers", governs the macroscopic features of the twist-bend nematic: textures, field effects, surface anchoring, etc. Moreover, the long range elasticity can be derived from the local elastic properties in a coarse-grained approach, as demonstrated before for the cholesteric phase [25, 26]. This will afford a macroscopic test of the microscopic elastic models, e.g. by experiments involving field- and temperature-induced texture transitions.

In this article, we develop a coarse-grained elastic model for the N_{TB} phase consisting of achiral bent-shaped molecules. We show that on a scale much larger than the period of the spontaneously distorted twist-bend nematic structure, the twist-bend nematic has the same symmetry, namely D_∞, as the SmA* phase. By analogy

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with de Gennes' [27] complex smectic order parameter ψ, we introduce a complex order parameter σ for the N_{TB} phase, with amplitude related to the heliconical tilt angle and phase defined by the displacement of the N_{TB} pseudo-layers from their equilibrium positions. By symmetry, we argue that the macroscopic elastic energy of the N_{TB} phase is analogous to the Landau - de Gennes energy of the SmA*.

To calculate the coarse-grained elastic constants and characteristic lengths, we adopt one of the local elasticity models, proposed so far for the N_{TB} phase. Averaging the local energy over one N_{TB} period, we obtain the macroscopic elastic constants in terms of a few experimentally accessible Frank-like nematic elastic coefficients. We show that the anisotropy of the elastic properties and their temperature dependence are substantially different from their smectic analogues. Moreover, we show that the N_{TB} pseudo-lamellar arrangement is chirally frustrated due to the structural chirality of the phase and we predict the existence of twist-bend nematic phases with TGB-like macroscopic structure.

Model

N_{TB} / SmA* analogy and coarse-grained elastic model of the twist-bend nematic phase

The structure of the N_{TB} phase (Fig. 1(a)) constituted by achiral bent-shaped molecules has been theoretically predicted long ago [14-17] and was experimentally confirmed recently [9-13]. As any other nematic phase, the twist-bend nematic presents only orientational long-range order, with the main axis **L** of the molecule oriented on average along the director **n**, the macroscopic symmetry axis of the phase. There is no long-range positional order and the centre-of-mass distribution of the molecules is random, in contrast to the mass-density wave in smectic phases (Fig. 1(b)). However, the most striking feature of the N_{TB} phase is the spontaneous distortion of the director: instead of remaining uniform, $\nabla \mathbf{n} \equiv \mathbf{0}$, as in most other mesophases with achiral building blocks, the director **n** is periodically distorted in the ground-state of the N_{TB} phase (Fig. 1(a)), $\mathbf{n}(z) = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, and the molecules are organized in a short-pitch conical helix with period $p \approx 10$ nm [10-12]. Here θ is the conical tilt angle of the director and $\varphi = q_0 z$ is the azimuthal angle, or phase, of the heliconical precession of the director around the helix axis **z**, with wave-vector $\mathbf{q}_0 = q_0\mathbf{z}$, $q_0 = \pm 2\pi/p$. The chiral symmetry of the N_{TB} phase is broken: the helix can be right-handed or left-handed, depending on the sign of the pseudo-scalar q_0, and both of these structures are ground-states of the N_{TB} phase (with the same energy).

Due to the low symmetry of the bent-shape molecules and to the strong heliconical distortion of the director, the N_{TB} phase has very low local symmetry, with additional biaxial and polar long-range orientational order [17, 19]. For this reason, we can expect that on length scale $\Lambda < p$ most of the properties of the twist-bend nematic, e.g. its elastic behaviour, will be different from the properties of other mesophases with periodic structure and higher symmetry, e.g. the cholesteric and the SmA* phases. However, at large scale, $\Lambda >> p$, the twist-bend nematic recovers the usual D_∞ symmetry point group of the N* and SmA* phases. For example, due to the short pitch, $p << \lambda$ (λ being the wavelength of light), the optic axis **N** of the N_{TB} phase is not along **n**, but along the macroscopic average of **n** over a few periods, i.e. **N** is a unit vector parallel to the helix axis [10, 28]. At macroscopic scale, $\Lambda >> p$, the optic axis **N** is a C_∞ symmetry axis of the N_{TB} phase and the twist-bend nematic belongs to the same D_∞ symmetry point group as the SmA*. Moreover, these two phases have the same translational symmetry since both of them are periodic in one-dimension, and with very short pitch. For symmetry reasons, we then expect that some of the macroscopic properties of the two phases will be similar. Actually, a number of observations show that this is indeed the case for the macroscopic elastic properties. In fact, the typical textures of unaligned N_{TB} samples (Fig. 1(c)) are strikingly similar to the usual focal-conic domains commonly observed in SmA, SmA* (Fig. 1(d)) and short-pitched N* phases. Another example is the recently reported [29] fast polar electro-optic effect in the N_{TB} phase, which is an exact analogue [10] of the well-known electroclinic effect [30] in the SmA* phase. Both the textures and the electrooptic response strongly depend on the macroscopic elastic properties of the phase, indicating that the macroscopic elasticity of the N_{TB} phase can be treated by analogy with the well understood elasticity of smectics.

Let us consider the unperturbed state of the chiral smectic A phase, SmA*. It is uniaxial, with optic axis along the director $\mathbf{n}_0$, and has a lamellar structure: the mass density ρ is modulated along the **z**-axis ($\mathbf{z} \| \mathbf{n}_0$), with wave vector $\mathbf{q}_0 = q_0\mathbf{n}_0$, where $q_0 = 2\pi/d$ (d is usually close to the molecular length). In the distorted SmA*, the director **n**(**r**) and the positions of the layers vary slowly in space (Fig. 2(a)). In his seminal paper [27] about the smectic – superconductor analogy, de Gennes proposed a complex smectic order parameter $\psi = |\psi|\exp(i\phi)$, where $|\psi|$ is the amplitude of the mass-density wave and the phase ϕ describes the local layer displacement, $u = d\phi/2\pi$, which varies slowly in space. For small distortions $\delta\mathbf{n} = \mathbf{n} - \mathbf{n}_0$, the most general energy density compatible with the SmA* symmetry is [26]

$$f_{smA^*} = A|\psi|^2 + \frac{1}{2}B|\psi|^4 + C_{\|}\left|\nabla_{\|}\psi\right|^2 + C_{\perp}\left|(\nabla_{\perp} - iq_0\delta\mathbf{n})\psi\right|^2 + \frac{1}{2}\left[K_{11}\mathbf{s}^2 + K_{22}(t - t_0)^2 + K_{33}\mathbf{b}^2\right] \quad , \quad (1)$$

Here A and B define the smectic "condensation" energy, favouring the density modulation for $A < 0$; the C-terms, with $\nabla_{\|} = (0, 0, \partial/\partial z)$ and $\nabla_{\perp} = (\partial/\partial x, \partial/\partial y, 0)$, describe the anisotropic "gradient" energy forbidding fast variation of ψ; K_{ii} are the Frank-Oseen elastic constants [31] for splay $\mathbf{s} = \mathbf{n}(\nabla\cdot\mathbf{n})$, twist $t = \mathbf{n}\cdot(\nabla\times\mathbf{n})$ and bend $\mathbf{b} = \mathbf{n}\times(\nabla\times\mathbf{n})$ distortions, and the pseudo-scalar t_0 describes the spontaneous twist of the nematic, due to the molecular chirality.

In the N_{TB} phase, the density is uniform but the order parameter tensor **Q**, and hence **n**, rotates along the z direction. The equilibrium N_{TB} structure corresponds to a circularly polarized tensorial wave, with amplitude $\sin\theta_0$ and phase $\varphi = q_0 z$. The

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surfaces described by $\varphi = 2\pi m$, with m integer, define a set of equidistant "pseudo-layers", corresponding to the same orientation of the director projection on the pseudo-layer. In the distorted N_{TB} structure, both the amplitude $\sin\theta(\mathbf{r})$ and the phase $\varphi(\mathbf{r})$ are functions of the position (Fig. 2(b)). By analogy with the SmA*, when $\delta\theta(\mathbf{r}) = \theta(\mathbf{r}) - \theta_0$, $\delta\varphi(\mathbf{r}) = \varphi(\mathbf{r}) - q_0 z$ and their gradients are small, we can define a complex N_{TB} order parameter $\sigma(\mathbf{r}) = \sin\theta(\mathbf{r})\exp(i\delta\varphi(\mathbf{r}))$, describing the heliconical tilt and the displacement of the pseudo-layers. Moreover, similar to the smectic case, in the ground-state of the N_{TB} phase, the optic axis $\mathbf{N} = \mathbf{N}_0$ is parallel to $\mathbf{q}_0$ and perpendicular to the pseudo-layers. In the distorted N_{TB} state, however, **N** can deviate from $\mathbf{N}_0$ by $\delta\mathbf{N} = \mathbf{N} - \mathbf{N}_0$, where $\delta\mathbf{N} \perp \mathbf{N}$ and $\delta\mathbf{N}^2 << 1$.

By analogy with the SmA*, substituting **n** with **N** and ψ with σ, we write the coarse-grained (CG) N_{TB} energy in the form

$$f_{TB}^{CG} = f_{TB}^{cond}(|\sigma|) + \gamma_{\|}\left|\nabla_{\|}\sigma\right|^2 + \gamma_{\perp}\left|(\nabla_{\perp} - iq_0\delta\mathbf{N})\sigma\right|^2 + \frac{1}{2}\left[K_{11}^{N}\left(\mathbf{s}^{N}\right)^2 + K_{22}^{N}((t^{N})^2 - 2t_0^{N}t^{N}) + K_{33}^{N}\left(\mathbf{b}^{N}\right)^2\right] \quad (2)$$

where K_{ii}^{N} are the elastic constants for splay $\mathbf{s}^{N} = \mathbf{N}(\nabla\cdot\mathbf{N})$, twist $t^{N} = \mathbf{N}\cdot(\nabla\times\mathbf{N})$ and bend $\mathbf{b}^{N} = \mathbf{N}\times(\nabla\times\mathbf{N})$ distortions of **N**, and t_0^{N} describes the spontaneous twist of **N**, due to the structural chirality of the N_{TB} phase (see the discussion below). At the N_{TB} - N phase transition, $\sigma = \sin\theta = 0$ and $\mathbf{N} \equiv \mathbf{n}$, implying that $K_{ii}^{N} = K_{ii}$ (if the pretransitional fluctuations are neglected). The first term in eqn (2), which is independent of $\delta\varphi(\mathbf{r})$, is the condensation energy of the N_{TB} phase. Its coarse-grained derivation is unphysical: it is defined by the short-scale N_{TB} structure, with lower symmetry than the uniaxial CG symmetry. In fact, this term should be derived directly from the local elastic model (see next section).

Coarse-grained elastic constants and characteristic lengths calculated using an explicit local elastic model

The coarse-grained energy in eqn (2) is derived purely from symmetry arguments, without any assumption about the local elasticity. In this sense, it is very general and describes qualitatively the macroscopic elastic behaviour of the N_{TB} phase independently of the material parameters of the twist-bend compound. More quantitative results can be obtained by adopting an explicit local elastic model. Calculating the energy density on the microscopic scale and then averaging it over a few periods will relate the macroscopically measurable properties, e.g. elastic constants, to the local variables, e.g. to the microscopic Frank-Oseen-like elastic constants in our case. This approach is quite general and it can be applied to any macroscopic physical property in order to investigate the microscopic structure of the N_{TB} phase by classic macroscopic experiments. Indeed, we have already successfully applied it for the bent-shape dimer CB7CB in two particular cases, estimating its heliconical pitch from the N_{TB} phase "electroclinic" response [10], and measuring the temperature dependence of the heliconical tilt angle [28] by comparison of the birefringence measured in the N and N_{TB} phases. Moreover, applying the same CG approach using different local elastic models will provide a powerful test of these still debated models by simple macroscopic experiments.

Hereafter, we will adopt for the local elasticity the elastic-instability (or negative-elasticity) model of the N_{TB} phase [17]. Let us consider a nematic phase formed by achiral bent-shaped molecules. As usual, the nematic order is described by the tensor $Q_{ij} = S(3n_i n_j - \delta_{ij})/2$, where S is the scalar order parameter [26]. At constant S, the distortion energy density of the nematic is

$$f_{FO} = \frac{1}{2}\left[K_{11}\mathbf{s}^2 + K_{22}t^2 + K_{33}\mathbf{b}^2\right], \quad (3)$$

where the elastic coefficients K_{ii} are positive, imposing uniform ground-state. The elastic-instability model [17] suggests that, for strongly bent molecules, K_{33} *decreases* with decreasing temperature, and even becomes *negative*. This pathological behaviour, confirmed now both experimentally [12, 32, 33] and theoretically [34-36], results in spontaneous bend of the director. For $K_{33} < 0$, high-order gradient terms are needed in the energy, to bound it from below [17]. In the simplest case of one-dimensional variation of **n**, **n** = **n**(z), the distortion energy is minimized for a twist-bend heliconical structure of the director field. At equilibrium, the tilt angle $\theta = \theta_0$ is constant, defined by $\sin^2\theta_0 = -K_{33}/(3K_{22})$ and the phase φ is $\varphi(z) = \mathbf{q}_0\cdot\mathbf{z} = q_0 z$, where the wave vector $\mathbf{q}_0 = \nabla\varphi(z)$ is defined by $\mathbf{q}_0{}^2 = q_0{}^2 = -K_{33}/(3C)$, and $C > 0$ is a fourth order elastic constant (for more details see [17] and ESI).

To calculate (see ESI) the condensation energy $f_{TB}^{cond}(|\sigma|)$ from the elastic-instability model we assume a small uniform deviation of θ, $\delta\theta << 1$, from the equilibrium tilt-angle value $|\sigma_0| \approx \theta_0$:

$$f_{TB}^{cond}(|\sigma|) = f_{TB}^{cond}(|\sigma_0|) + K_{\delta\sigma}\delta\sigma^2 \approx \frac{1}{6}K_{33}q_0{}^2\theta_0{}^2 - \frac{2}{3}K_{33}q_0{}^2\delta\theta^2 \quad (4)$$

Here and further on, for the sake of simplicity, we suppose $\delta\theta^2 << \theta_0{}^2 << 1$ and we neglect high-order terms in $\theta_0{}^2$.

The CG energy coefficients can be obtained from the local distortion energy considering a few simple particular cases. We first consider a uniform compression of the pseudo-layers, defined by $|\sigma| \equiv |\sigma_0|$, $\delta\mathbf{N} \equiv 0$ and $q = q_0 + \delta q = \text{const}$. Comparing the exact local energy, $\delta f_{loc}(\delta q) = -(2/3)K_{33}\theta_0{}^2\delta q^2$, with the CG result $\delta f_{CG}(\delta q) = \gamma_{\|}\theta_0{}^2\delta q^2$, we obtain directly $\gamma_{\|} = -2K_{33}/3$.

For $\gamma_{\perp}$, we consider a uniform tilt of **N** with respect to **q** by a small angle α, with $\delta\mathbf{N} = (0,\alpha,0)$, $|\sigma| \equiv |\sigma_0|$ and $\delta\varphi \equiv 0$. The CG distortion energy is: $\delta f_{CG}(\alpha) = \gamma_{\perp}\theta_0{}^2 q_0{}^2\alpha^2$. The local distortion energy, obtained (see [10] and ESI) by averaging over one period of

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the heliconical structure, is: $\delta f_{loc}(\alpha) = K_{\delta N}\alpha^2/2$, where $K_{\delta N} = (K_{11}+K_{22})\theta_0{}^2 q_0{}^2/2$, and we obtain $\gamma_\perp = (K_{11}+K_{22})/4$.

To calculate K_{ii}^N and t_0^N, we assume again $|\sigma| \equiv |\sigma_0|$, $\delta\varphi \equiv 0$ and $\delta\mathbf{N} = (0, \alpha(\mathbf{r}), 0)$, where $\alpha(\mathbf{r})$ is a slowly varying function, $p|\nabla\alpha| << 1$. We consider separately the cases with $\nabla\alpha$ parallel to the **x**, **y** or **z** axis (see Fig. 3), corresponding respectively to pure twist, splay, and bend distortions of **N**. Averaging the excess energy over one period, we obtain it as a sum of three terms (see ESI), proportional respectively to α^2, $d\alpha/dx_i$ and $(d\alpha/dx_i)^2$, where $x_i = x, y, z$. The α^2 term gives again $\gamma_\perp$, and the terms linear in $d\alpha/dx_i$ vanish for $x_i = y, z$, as in the usual nematic phase [31]. The comparison of the other terms with eqn (2) gives:

$$t_0^N = q_0\theta_0{}^2 \; ; \; K_{11}^N = K_{11} \; ; \; K_{22}^N = K_{22} \; ; \; K_{33}^N = K_{33} + \frac{1}{2}(K_{11}+K_{22})\theta_0{}^2 \quad (5)$$

The K_{33}^N constant is negative and we can expect, by analogy, a *spontaneous bend of the optic axis* **N** in the N_{TB} phase, superimposed on the heliconical distortion of the director **n**. However, this analogy is spurious (see ESI), due to the $\gamma_\perp$ term in eqn (2), which makes the tilt of **N** very costly. Indirectly, the $\gamma_\perp$ term also forbids any large twist or bend of **N**, as only distortions with $\mathbf{q}=\nabla\varphi \approx q_0\mathbf{N}$ are allowed. Then, $\nabla\times\mathbf{N} \approx \nabla\times\nabla\varphi/q_0 \equiv \mathbf{0}$, i.e. the twist and bend (but not the splay) of **N** are expelled from the N_{TB} phase, exactly as the twist and bend of **n** are expelled from the SmA [27]. Moreover, by analogy with the N - SmA transition [27], we expect a pretransitional divergence of K_{22} and K_{33} close to the N - N_{TB} transition.

As in the smectic case [37], far from the boundary surfaces and defects the coarse-grained N_{TB} energy can be further simplified, taking into account that $|\sigma| \equiv |\sigma_0|$ and $\mathbf{N} \| \mathbf{q}$. The energy density then becomes a function of the "layer" compression only, $\varepsilon = \delta q/q_0$, and the principal radii of curvature of the pseudo-layers, R_1 and R_2:

$$f_{TB}^{CG} = \frac{1}{2}\bar{B}\varepsilon^2 + \frac{1}{2}K_{11}^N\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 \quad (6)$$

Here $\bar{B} = 2\gamma_\parallel q_0{}^2\sin^2\theta_0 \approx -4K_{33}q_0{}^2\theta_0{}^2/3$ is the compression modulus of the layers and we omitted the surface-like term related to the Gaussian curvature. Like in smectics, when the assumption $\Lambda >> p$ is satisfied, eqn (6) is valid even for strongly distorted pseudo-layers (e.g. in the focal conic domains).

The CG energy describes both the amplitude and the relaxation length of the distortions. Let us consider a small deviation of the heliconical tilt angle, $\delta\theta(0) = \theta_s - \theta_0$, imposed by a boundary surface (Fig. 4). Deep in the sample, the deviation vanishes, $\delta\theta(\infty) = 0$. Minimizing the excess energy due to $\delta\theta(\mathbf{r})$, we obtain the (anisotropic) coherence lengths of the N_{TB} phase:

$$\xi_\parallel = \sqrt{\frac{\gamma_\parallel}{K_{\delta\sigma}}} = \frac{1}{q_0} \; ; \; \xi_\perp = \sqrt{\frac{\gamma_\perp}{K_{\delta\sigma}}} = \frac{1}{q_0\theta_0}\sqrt{\frac{K_{11}+K_{22}}{8K_{22}}} >> \frac{1}{q_0}. \quad (7)$$

These lengths are meaningful in the CG model. Actually, the large value of $\xi_\perp$, $\xi_\perp q_0 >> 1$, justifies *a posteriori* the CG averaging over one period, used for the derivation of $\gamma_\perp$. On the contrary $\xi_\parallel = 1/q_0$ is an *exact* result, as both $\gamma_\parallel$ and $K_{\delta\sigma}$ are derived directly from the local distortion energy, without any CG approximation.

To estimate the penetration lengths for the main distortions of **N**, we consider a small tilt $\delta\mathbf{N}$ imposed at the boundary, relaxing inside a N_{TB} sample with almost perfect structure, $|\sigma| \equiv |\sigma_0|$ and $\mathbf{q} \equiv \mathbf{q}_0$. Three different geometries are possible (see Fig. S1), corresponding respectively to splay, twist and bend of **N**. In all cases, the energy due to $\delta\mathbf{N} \neq 0$ is $\gamma_\perp q_0{}^2\sin^2\theta_0\delta\mathbf{N}^2 > 0$. For $i = 1, 2$, the gradient energy is $K_{ii}^N(d\delta\mathbf{N}/dx_i)^2/2 > 0$, and $\delta\mathbf{N}$ relaxes exponentially with characteristic lengths:

$$\lambda_1 = \sqrt{\frac{K_{11}^N}{2\gamma_\perp q_0{}^2\theta_0{}^2}} = \frac{1}{q_0\theta_0}\sqrt{\frac{2K_{11}}{K_{11}+K_{22}}},$$

$$\lambda_2 = \sqrt{\frac{K_{22}^N}{2\gamma_\perp q_0{}^2\theta_0{}^2}} = \frac{1}{q_0\theta_0}\sqrt{\frac{2K_{22}}{K_{11}+K_{22}}} \quad (8)$$

In both cases, $\lambda_i \approx 1/q_0\theta_0 >> 1/q_0$, justifying *a posteriori* the CG approximations.

The bend case is more complicated, due to $K_{33}^N < 0$. Including a fourth order term in the distortion energy of the optic axis **N**, we obtain a solution (see ESI) which is a damped oscillation with large wave vector, $k_3 \approx q_0$, and short relaxation length $\lambda_3 \approx 2/q_0$. This result is obviously incompatible with the CG approach, forbidding strong gradients of the macroscopic variables. Therefore, the case of a bend distortion of **N** should be treated directly with the local elastic model, avoiding the CG approximation.

Anisotropy and temperature dependence of the coarse-grained elastic parameters

Except for λ_3, our CG results are qualitatively similar to the SmA case: the twist and bend distortions of **N** are forbidden and expelled from the bulk, the deviations from the condition $\mathbf{q} = q_0\mathbf{N}$ are energetically very costly, etc. Quantitatively, however, the smectic and the coarse-grained results are very different. For example $\xi_\parallel >> \xi_\perp$ in smectics [38, 39], while for the N_{TB} phase $\xi_\parallel/\xi_\perp = \sqrt{\gamma_\parallel/\gamma_\perp} = \sqrt{8/3}\theta_0 << 1$, i.e. the anisotropy is reversed. In consequence, the N_{TB} "clusters" in the nematic phase, due to pretransitional fluctuations, will have an oblate shape, whereas the smectic "clusters" are prolate. Similarly, the shape of the edge dislocation cores will be different: in both phases, the melted core

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of an edge-dislocation is expected to have an elliptical shape, with semi-axes $\xi_{\parallel}$ and $\xi_{\perp}$; however, in the SmA* case, the long axis $\xi_{\parallel}$ is perpendicular to the layers, whereas in the N_{TB} case, the long axis $\xi_{\perp}$ is parallel to the pseudo-layers. We also expect that in the N_{TB} phase the core energy of the edge-dislocations will be smaller than that of the screw-dislocations, due to their cross-sections, proportional respectively to $\xi_{\parallel}\xi_{\perp}$ and $\xi_{\perp}^{2}$, that are smaller for the former. However, these qualitative predictions must be taken with caution because the structure within the melted core might be different from the intuitively expected uniform nematic, as recently suggested for the planar defects separating two monochiral N_{TB} domains [28]. We note also that the ratio $\xi_{\parallel}/\xi_{\perp}$, which is constant for the SmA, is temperature-dependent in the N_{TB} phase, due to $\theta_0 \sim \sqrt{T^*-T}$. The N_{TB} compression modulus also has an unusual temperature dependence, $\bar{B} \sim \theta_0^{4} \sim (T^*-T)^2$, which is much faster than for the SmA ($\bar{B} \sim T^*-T$), and becomes extremely soft close to the N – N_{TB} transition temperature T*. These features are related to the "negative elasticity" model adopted here, giving a *temperature-dependent* coefficient $\gamma_{\parallel} \sim T^*-T$, which is not expected in some of the proposed local elastic models. Therefore, the measurement of the temperature dependences of macroscopic properties, e.g. $\bar{B}$ and θ_0, will be an efficient test of the N_{TB} local elastic models.

The spontaneous twist of the optic axis, $t_0^{N} = q_0\theta_0^{2}$, is also drastically different from the SmA* case: it is due to the N_{TB} chiral structure (the heliconical distortion of **n**), and not to the molecular chirality. As expected by symmetry, t_0^{N} is a pseudo-scalar: its sign, as the sign of $q_0 = d\varphi/dz$, is inversed in a mirror image. Moreover, in the N* and SmA* cases, t_0 is almost temperature-independent and continuous at the N* - SmA* transition whereas t_0^{N} varies with the temperature as $(T^*-T)^{3/2}$, and vanishes in the N phase.

Type I versus Type II behavior and TGB-like structure of the N_{TB} phase

The twist-bend nematic is frustrated by the chiral field $h = K_{22}^{N} t_0^{N}$, expelled from the bulk. By analogy with the SmA* [27] and with superconductors, two kinds of coarse-grained N_{TB} behaviour are expected, depending on the value of the Ginsburg parameter $k_t = \lambda_2/\xi_{\perp}$. For $k_t \le 1/\sqrt{2}$, we expect *type I* behaviour: for strong enough chiral field $h \ge h_c$, the bulk N_{TB} order melts, $\theta_0 \equiv 0$. For $k_t > 1/\sqrt{2}$, *type II* behaviour is expected: above a critical value h_{c1}, the twist field penetrates in the "layered" N_{TB} structure through a network of screw dislocations of the pseudo-layers, forming Twist Grain Boundaries (TGB). Then, we expect a TGB_{NTB} phase, a twist-bend nematic analogue of the TGB_A phase [40]. Our CG result $k_t = 4K_{22}/(K_{11}+K_{22}) \approx 4/3$, corresponds to a moderate *type II* behavior of the N_{TB} phase. Moreover, assuming $k_t >> 1/\sqrt{2}$ we obtain $h > h_{c1}$ (see ESI), indicating that the twist-bend nematic has TGB_{NTB} structure *at any temperature*. Detailed analysis of the TGB_{NTB} phase, considering moderate k_t values and the structure of the N_{TB} screw dislocations, will be presented elsewhere.

Comparison with previously reported experimental data

The symmetry-based CG energy (2) is independent of the choice of a local elastic model which is only required for the calculation of the coefficients. The "negative-elasticity" model adopted here gives most of the CG energy coefficients (except for K_{33}^{N} and λ_3) as a function of the measurable quantities K_{11}, K_{22}, q_0 and θ_0. For CB7CB, the most studied compound in this context, $K_{11} \approx 5$ pN, $p \approx 8$ nm and $\theta_0 \approx 9°$ at the N - N_{TB} transition [10-12, 28]. Assuming $K_{22} \approx K_{11}/2$, we obtain $\gamma_{\parallel} = 0.12$ pN, $\gamma_{\perp} = 1.9$ pN, $\xi_{\parallel} = 0.8$ nm, $\xi_{\perp} = 3.1$ nm, $\lambda_1 = 5.9$ nm, $\lambda_2 = 4.2$ nm and $\bar{B} = 3800$ Pa. Our estimation of the compression modulus agrees qualitatively with the value $\bar{B} = 2000$ Pa, reported for a different compound from previous experiments and coarse-grained models [23, 24], based on a different local elasticity. We expect that future experiments with improved precision and CG theories based on different microscopic mechanisms will provide valuable test of the validity of the N_{TB} local elastic models proposed so far, which are still a controversial issue. We note that our CG model, after straightforward extension to cover the cases of external fields and surface-imposed constraints, will greatly simplify the interpretation of future macroscopic experiments. Actually, a similar approach provided an excellent electro-optical estimation of the heliconical pitch of the dimer CB7CB [10] shortly before its more direct freeze-fracture measurements [11, 12].

Some of our results are qualitatively similar to the recently proposed Landau model for the N_{TB} phase [18]. Actually, both models are based on the uniaxial large-scale symmetry of the phase and introduce almost identical complex order parameters, respectively σ and φ. However, we exploit explicitly a local elastic model relating the CG energy coefficients to measurable constants, facilitating experimental tests. Moreover, the temperature dependences of most of the energy terms are quite different for the two models, as *both* θ_0^2 and q_0^2 are proportional to *T-T** in our case [17], while q_0 is constant in the Landau model [18].

Conclusion

We have demonstrated that, at the macroscopic scale, the twist-bend nematic phase has the same symmetry as the SmA* phase: both these phases show one-dimensional periodic structure, with pitch of a few nanometers; both are chiral because of the molecular chirality of the SmA* and the doubly degenerate heliconical organization of the achiral bent-shaped molecules in the N_{TB} phase; and both phases possess a C_∞ symmetry axis, the director **n** for the SmA* and the macroscopic optic axis **N** for the N_{TB} phase. We proposed an N_{TB} / SmA* analogy and by considering a complex order parameter, the N_{TB} analogue of the de Gennes smectic order parameter ψ, we proposed a general expression for the macroscopic elastic energy density of the N_{TB} phase. Adopting the "elastic-instability" local elastic model of the N_{TB} phase and averaging the energy density over a few periods of the N_{TB}

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structure, we obtained the macroscopic elastic constants as functions of a few microscopic elastic parameters. Our CG approach may be useful for the treatment of the macroscopic experimental results in terms of the existing local elastic models and for the test of the validity of these models.

Despite the qualitative analogy, we showed that the anisotropy and the temperature dependence of the macroscopic elastic properties of the N_{TB} phase are quite different from those of the SmA*. We argued that this may result in drastically different geometry and energy balance of the dislocations and other defects of the N_{TB} phase compared to their SmA* analogues. Finally, we demonstrated that the N_{TB} phase is macroscopically frustrated due to its chiral symmetry breaking and that this can lead to phases with large density of screw dislocations, analogues of the TGB phases of the rod-like smectogens and of the Shubnikov phase of the Type II superconductors.

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References

1. T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi and H. Takezoe, *Journal of Materials Chemistry*, 1997, **7**, 1307-1309.
2. T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *Journal of Materials Chemistry*, 1996, **6**, 1231-1233.
3. J. Harden, B. Mbanga, N. Éber, K. Fodor-Csorba, S. Sprunt, J. T. Gleeson and A. Jákli, *Physical Review Letters*, 2006, **97**, 157802.
4. G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, *Journal of Materials Chemistry*, 2002, **12**, 2591-2593.
5. M. Sepelj, A. Lesac, U. Baumeister, S. Diele, H. L. Nguyen and D. W. Bruce, *Journal of Materials Chemistry*, 2007, **17**, 1154-1165.
6. C. Prasang, A. C. Whitwood and D. W. Bruce, *Chem. Commun.*, 2008, DOI: 10.1039/b719555a, 2137-2139.
7. V. Goertz, C. Southern, N. W. Roberts, H. F. Gleeson and J. W. Goodby, *Soft Matter*, 2009, **5**, 463-471.
8. V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis and G. H. Mehl, *Phys.Rev. Lett.*, 2010, **105**, 167801.
9. M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi and H. Zimmermann, *Physical Review E*, 2011, **84**, 031704.
10. C. Meyer, G. R. Luckhurst and I. Dozov, *Physical Review Letters*, 2013, **111**, 067801.
11. D. Chen, J. H. Porada, J. B. Hooper, A. Klittnick, Y. Shen, M. R. Tuchband, E. Korblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. Maclennan and N. A. Clark, *PNAS*, 2013, **110**, 15931-15936.
12. V. Borshch, Y. K. Kim, J. Xiang, M. Gao, A. Jakli, V. P. Panov, J. K. Vij, C. T. Imrie, M. G. Tamba, G. H. Mehl and O. D. Lavrentovich, *Nat. Commun.*, 2013, **4**, 2635
13. D. Chen, M. Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba, M. A. Glaser, J. E. Maclennan and N. A. Clark, *Physical Review E*, 2014, **89**, 022506.
14. R. B. Meyer, in *Molecular Fluids*, eds. R. Balian and G. Weill, Gordon and Breach, New York 1976, vol. XXV-1973 of *Les Houches Summer School in Theoretical Physics*, pp. 273 - 373.
15. V. L. Lorman and B. Mettout, *Physical Review Letters*, 1999, **82**, 940-943.
16. V. L. Lorman and B. Mettout, *Physical Review E*, 2004, **69**, 061710.
17. I. Dozov, *EPL (Europhysics Letters)*, 2001, **56**, 247-253.
18. E. I. Kats and V. V. Lebedev, *Jetp Letters*, 2014, **100**, 110-113.
19. S. M. Shamid, S. Dhakal and J. V. Selinger, *Physical Review E*, 2013, **87**, 052503.
20. E. G. Virga, *Physical Review E*, 2014, **89**, 052502.
21. G. Barbero, L. R. Evangelista, M. P. Rosseto, R. S. Zola and I. Lelidis, *Phys. Rev. E*, 2015, **92**, 030501.
22. I. Lelidis and G. Barbero, *Liquid Crystals*, 2015, DOI: 10.1080/02678292.2015.1078917
23. P. K. Challa, V. Borshch, O. Parri, C. T. Imrie, S. N. Sprunt, J. T. Gleeson, O. D. Lavrentovich and A. Jakli, *Physical Review E*, 2014, **89**, 060501.
24. S. M. Salili, C. Kim, S. Sprunt, J. T. Gleeson, O. Parri and A. Jakli, *Rsc Advances*, 2014, **4**, 57419-57423.
25. T. C. Lubensky, *Physical Review A*, 1972, **6**, 452-470.
26. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon, Oxford, 1994.
27. P. G. de Gennes, *Solid State Communications*, 1972, **10**, 753-756.
28. C. Meyer, G. R. Luckhurst and I. Dozov, *Journal of Materials Chemistry C*, 2015, **3**, 318-328.
29. V. P. Panov, R. Balachandran, M. Nagaraj, J. K. Vij, M. G. Tamba, A. Kohlmeier and G. H. Mehl, *Applied Physics Letters*, 2011, **99**, 261903.
30. S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, 1977, **38**, 848-851.
31. F. C. Frank, *Discussions of the Faraday Society*, 1958, **25**, 19-28.
32. K. Adlem, M. Copic, G. R. Luckhurst, A. Mertelj, O. Parri, R. M. Richardson, B. D. Snow, B. A. Timimi, R. P. Tuffin and D. Wilkes, *Physical Review E*, 2013, **88**, 022503.
33. R. Balachandran, V. P. Panov, J. K. Vij, A. Kocot, M. G. Tamba, A. Kohlmeier and G. H. Mehl, *Liquid Crystals*, 2013, **40**, 681-688.
34. M. Cestari, E. Frezza, A. Ferrarini and G. R. Luckhurst, *Journal of Materials Chemistry*, 2011, **21**, 12303-12308.
35. C. Greco, G. R. Luckhurst and A. Ferrarini, *Soft Matter*, 2014, **10**, 9318-9323.
36. C. Greco, A. Marini, E. Frezza and A. Ferrarini, *ChemPhysChem*, 2014, **15**, 1336-1344.
37. M. Kleman and O. D. Lavrentovich, *Soft Matter Physics: An Introduction*, Springer, New York, 2003.
38. J. Als-Nielsen, R. J. Birgeneau, M. Kaplan, J. D. Litster and C. R. Safinya, *Physical Review Letters*, 1977, **39**, 352-355.
39. S. Sprunt, L. Solomon and J. D. Litster, *Physical Review Letters*, 1984, **53**, 1923-1926.

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40. S. R. Renn and T. C. Lubensky, *Phys Rev A*, 1988, **38**, 2132-2147.

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Figure Captions

Fig. 1. Structure of the N_{TB} and SmA* phases. (a) In the N_{TB} phase, the achiral bent-shaped molecules are organized on a conical helix with short pitch $p \approx 10$ nm. The nematic director **n** is tilted at angle θ with respect to the helix axis **z**. The planes corresponding to the same projection of **n** on the **xy**-plane form a set of equidistant "pseudo-layers" of the periodic N_{TB} phase. This ground state is chiral, with doubly degenerate handedness. At macroscopic scale, the state is uniaxial, with C_∞ axis along the optic axis **N**, which is the macroscopic average orientation of **n** over several periods. Locally, the symmetry of the phase is much lower, with additional local biaxial and polar orders: the "long" molecular axis **L** is preferentially oriented along the heliconically precessing director **n**; the "bow" axis **B** is on average parallel to the bend vector **b**, which rotates on a helix. (b) In the SmA*, the center-of-mass density of the molecules is periodically modulated along the nematic director **n**. The molecules are organized in layers perpendicular to **n**, which is also a C_∞ symmetry axis of the phase. The SmA* phase is chiral due to the molecular chirality. (c) The typical macroscopic texture of the N_{TB} phase (free drop of CB7CB, T=75 °C) is the focal conic texture, which is optically undistinguishable from the focal conics in the SmA, SmA* and N* phases. (d) Focal conic texture of a SmA* cell with untreated surfaces (8OCB, doped with 20.5 % S-811 by weight, T=62°C).

Fig. 2. Analogy between the SmA* and N_{TB} phases. (a) The undistorted SmA* layers (dashed lines) are equal-phase planes of the density wave ψ with wave vector $\mathbf{q}_0 = q_0\mathbf{n}_0$. In the distorted SmA*, the layers (solid lines) are displaced by $u(\mathbf{r})$ along **z** and the director $\mathbf{n}(\mathbf{r})$ is tilted. (b) The N_{TB} pseudo-layers are equal-phase surfaces of the heliconical precession of **n** around the optic axis **N**. In the distorted N_{TB}, the pseudo-layers are displaced and $\mathbf{N}(\mathbf{r})$ is tilted.

Fig. 3. Principal distortion modes of the N_{TB} optic axis **N**: twist (a), splay (b) and bend (c).

Fig. 4. Coherence lengths of the twist-bend nematic. The surface-imposed conical angle $\theta_s << \theta_0$ relaxes to its equilibrium value θ_0 in the bulk.

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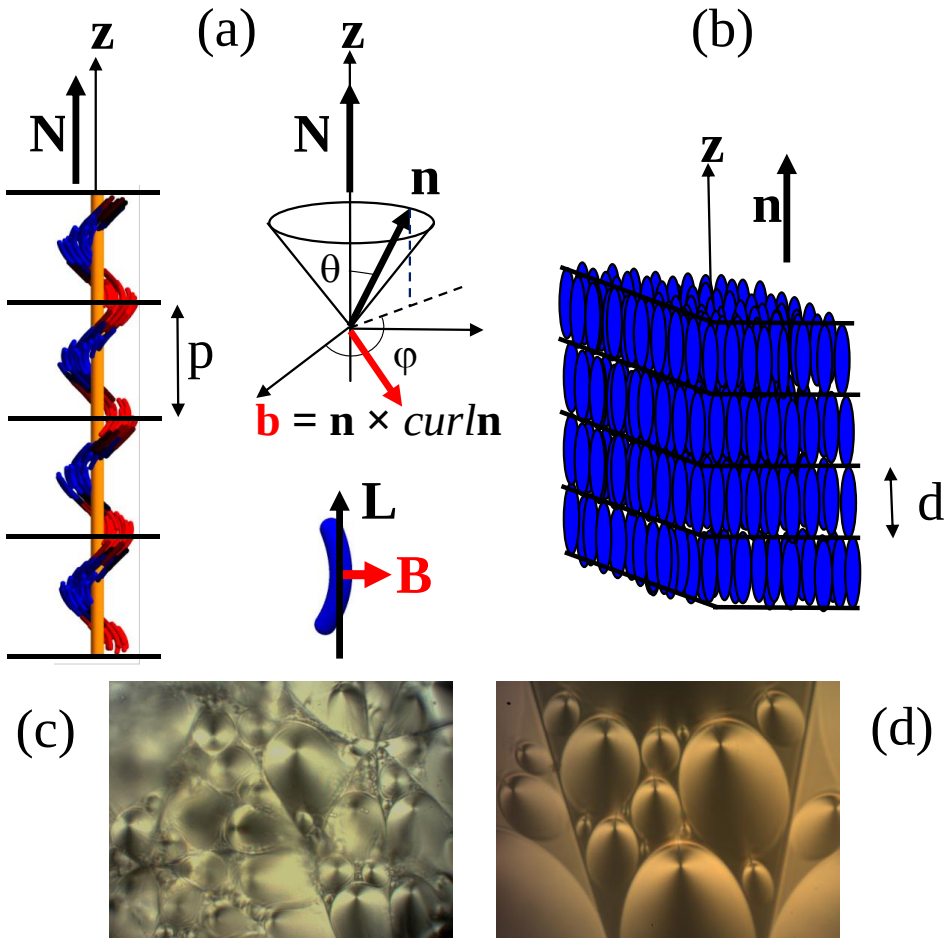

Fig. 1

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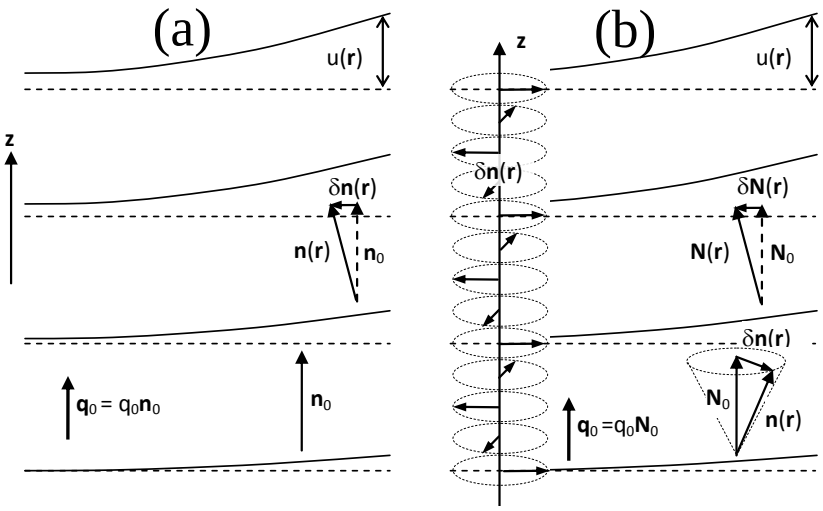

Fig. 2

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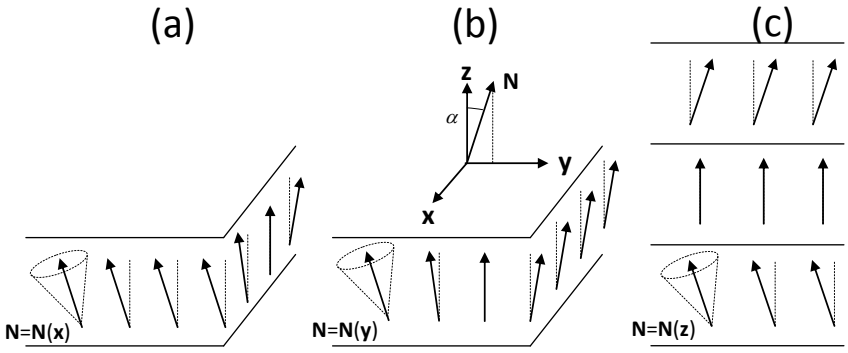

Fig. 3

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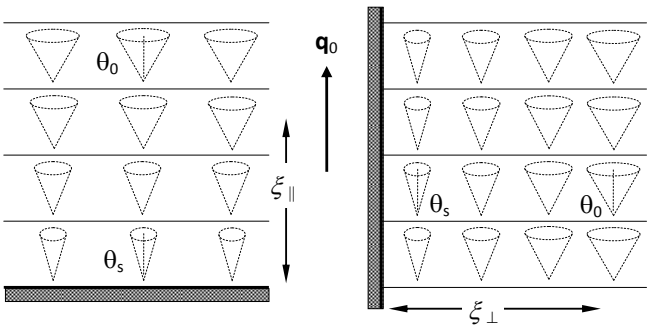

Fig. 4

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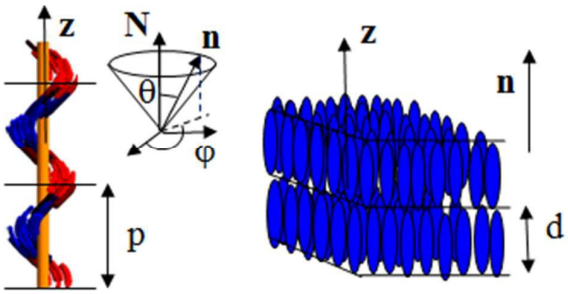
We develop a coarse-grained model describing the macroscopic elasticity of the Twist-Bend Nematic by analogy with the chiral smectic-A phase.



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