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Teresa Lopez-Leon, Alberto Fernandez-Nieves, Maurizio Nobili, Christophe Blanc. Nematic-Smectic Transition in Spherical Shells. *Physical Review Letters*, 2011, 106, pp.247802. <10.1103/PhysRevLett.106.247802>. <hal-00652863>

**HAL Id: hal-00652863**

**<https://hal.science/hal-00652863v1>**

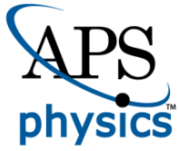
Submitted on 7 Jun 2021

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Phys. Rev. Lett. **106**, 247802 — Published 15 June 2011

DOI: [10.1103/PhysRevLett.106.247802](https://doi.org/10.1103/PhysRevLett.106.247802)

# Nematic-Smectic Transition in Spherical Shells

Teresa Lopez-Leon,<sup>1,\*</sup> Alberto Fernandez-Nieves,<sup>2</sup> Maurizio Nobili,<sup>1</sup> and Christophe Blanc<sup>1</sup>

<sup>1</sup>*Laboratoire Charles Coulomb(LCC), UMR5221, CNRS and Université Montpellier II,  
Place Eugène Bataillon, 34095 Montpellier, France.*

<sup>2</sup>*Georgia Institute of Technology, School of Physics,  
837 State St. NW, 30332 Atlanta GA, United States.*

We study the nematic-smectic phase transition of a thermotropic liquid crystal confined to a spherical shell. Far from the nematic-smectic phase transition temperature,  $T_{NS}$ , we observe a configuration with four  $+1/2$  defects, as predicted by theory. Since in this case  $K_1 \approx K_3$ , the four defects are confined at the thinnest part of the shell to minimize the energy associated to the defect cores. By contrast, near  $T_{NS}$ , where  $K_3 \gg K_1$ , bend distortions become prohibited and the defects organize themselves along a great circle of the sphere, confirming recent theoretical and simulation results. During this structural change, the defects associate in two pairs that behave independently. In the smectic phase, we observe a new configuration displaying curvature walls.

PACS numbers: 61.30.Jf, 61.30.Hn, 64.75.Xc

Nematic liquid crystals are typically formed by rod-like molecules displaying orientational order along an average direction,  $\mathbf{n}$ , called the director. When a nematic is confined to a spherical shell, the director field is necessarily disrupted by the presence of topological defects [1, 2]. These systems not only are rich systems to study topological problems, but they also provide a promising route for generating colloids with a valence [3], which is an important goal in material science [4]. Different defect structures have been observed, differing in the number and distribution of defects [5]. The associated elastic energy is given by the Frank-Oseen free energy density [6]:

$$f = \frac{1}{2}K_1(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2 \quad (1)$$

where  $K_1$  and  $K_3$  are the elastic constants associated to splay and bend distortions. In the limit of a very thin shell, the director can be regarded as a surface field, and thus, the twist term associated to  $K_2$  can be neglected. When  $K_1 = K_3$ , theory predicts a configuration with four defects arranged in a tetrahedral fashion [7], as shown in Fig.1(a). In this configuration, each defect has a topological charge  $s = +\frac{1}{2}$ , reflecting the  $\pi$  rotation experienced by  $\mathbf{n}$  along a path encircling each defect. This is consistent with a mathematical theorem due to Poincaré and Hopf, which establishes that the total topological charge for a nematic sphere is  $s = +2$  [8]. Interestingly, a new arrangement is expected when  $K_3 \gg K_1$ , in which the four  $s = +\frac{1}{2}$  defects are placed along a great circle of the sphere [9, 10], as shown in Fig.1(b). These theoretical expectations, however, have never been experimentally tested nor the effect of the anisotropy in the elastic constants been experimentally explored.

In this letter, we study the effect of the anisotropy in elastic constants  $K_1$  and  $K_3$  by taking advantage of the divergence of  $K_3$  near the nematic-smectic phase transition temperature,  $T_{NS}$  [11]. Due to the heterogeneous

thickness of the experimental shells, the four  $s = +\frac{1}{2}$  defects characteristic of the nematic phase appear confined in a small region of the shell and not arranged in a tetrahedral configuration. By decreasing the temperature toward  $T_{NS}$ , the defects progressively separate to eventually arrange themselves in a great circle. Below  $T_{NS}$ , the translational symmetry of the nematic phase is broken and a smectic shell is formed.

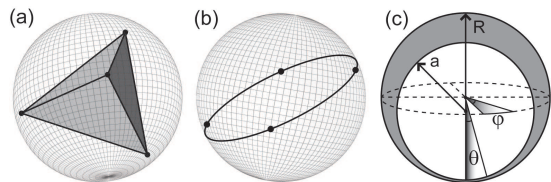


FIG. 1: Arrangement of four  $s = +\frac{1}{2}$  disclinations on a bi-dimensional shell (a) in a tetrahedral configuration when  $K_1 \approx K_3$ , and (b) along a great circle when  $K_1 \ll K_3$ . (c) Cross-section of an experimental shell with non-uniform thickness.

To fabricate the liquid crystal shells, we generate double emulsions in a microfluidic glass capillary device [12]. An inner aqueous droplet is encapsulated inside an outer liquid crystal droplet, as schematically shown in Fig.1-(c), which is in turn dispersed in a continuous aqueous phase. The average thickness of the shell,  $h$ , is given by the difference between the outer and inner radii,  $R - a$ . In our experiments,  $R$  is within the  $(30 - 120)\mu\text{m}$  range and  $h$  is typically  $(2 - 3)\%$  of  $R$ . The inner and outer phases contain 1 wt% of polyvinyl alcohol (PVA,  $M_w \sim 20,000 \text{ g mol}^{-1}$ ), which stabilizes the double emulsion and imposes planar degenerate anchoring to the liquid crystal. The middle phase is 4-n-octyl-4-cyanobiphenyl (8CB), a liquid crystal displaying a nematic-smectic phase transition at  $T_{NS} = 33.5^\circ\text{C}$ . Since the inner aqueous solution is slightly denser than 8CB, the inner droplet sinks inside the outer one, making the shell thinner at the bottom and thicker at the top. In terms of thickness, the ex-

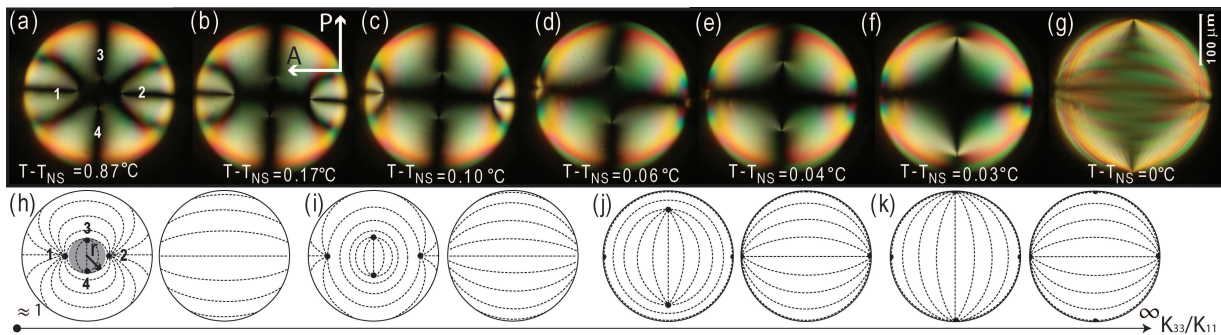


FIG. 2: (a-g) Cross-polarized images of a 8CB nematic shell as temperature  $T$  decreases toward the nematic-smectic phase transition temperature  $T_{NS}$ . (h-k) Evolution of the director field and defect structure during the process, in which  $K_3/K_1$  changes between  $1 < K_3/K_1 < \infty$ . Each panel shows the director field on the lower (left) and upper (right) hemispheres.

perimental shells are, thus, axisymmetric with respect to the gravity direction, with a non uniform thickness  $\delta \approx h(1 - \cos\theta)$  that depends on the zenithal angle  $\theta$  [Fig. 1(c)]. We fabricate and store the shells at  $37^\circ\text{C}$ , where 8CB is in the nematic phase. Due to the divergence of  $K_3$  at  $T_{NS}$ , an accurate control of temperature is required to guarantee a quasistatic approach to the nematic-smectic phase transition; we use a heating stage with a Lakeshore controller to regulate the temperature with a precision of  $0.01^\circ\text{C}$ . Additionally, after changing temperature, we wait for 20 minutes to ensure that the system is indeed in an equilibrium state.

Figure 2(a-g) shows the birefringence texture of a nematic shell with four defects as the temperature  $T$  is quasi-statically decreased toward  $T_{NS}$ . The evolution of the defect positions and director fields is represented in Fig.2(h-k). When  $T - T_{NS} \gtrsim 1^\circ\text{C}$ , the four defects appear confined at the bottom of the shell, as shown in Fig. 2(a). However, as  $T$  approaches  $T_{NS}$ , defects 1 and 2 start moving away from each other, while defects 3 and 4 only slightly increase their separation, as shown in Figs. 2(a-d). It is only after defects 1 and 2 reach the equatorial plane that defects 3 and 4 significantly move away from each other to eventually reach the equatorial plane too, as shown in Figs. 2(e-g). To quantify the evolution of the defect pairs, we plot the ratio between the angles subtended by defects 1-2 and 3-4 with respect to the center of the shell,  $\alpha_{12}$  and  $\alpha_{34}$ , as a function of  $T - T_{NS}$ . When  $T$  is far from  $T_{NS}$ , the defects are almost located at the vertices of a square and  $\alpha_{12} \approx \alpha_{34}$ , as shown in Fig. 3. Decreasing  $T$  causes the elongation of the structure into a rhombus with  $\alpha_{12} > \alpha_{34}$ . This elongation becomes maximum at  $T - T_{NS} = 0.06$ . Below this, defects 3-4 progressively migrate toward the equatorial plane. As a result,  $\alpha_{12}/\alpha_{34}$  decreases until eventually the defects are located in a great circle and  $\alpha_{12} \approx \alpha_{34}$  again, as shown in Fig. 3.

The  $\alpha_{12}/\alpha_{34}$  ratio is closely related to the evolution of  $K_3$  and  $K_1$  with  $T$ . Close to  $T_{NS}$ ,  $K_3$  diverges with respect to  $K_1$ , as shown in the inset of Fig.3(a), and thus,

bend distortions become energetically prohibited. This forces  $\mathbf{n}$  to align along great circles, which are the counterparts of straight lines on the sphere. In this configuration, schematically represented in Figs.2(k), the four defects are necessarily located on a great circle. For shells homogeneous in thickness, all great-circle arrangements are degenerated in energy. However, this degeneracy is broken in our experimental shells that are heterogeneous in thickness. In this case, the ground state is achieved when the four defects are located on the equatorial plane, along the only great circle in which  $\delta$  is uniform.

Far from  $T_{NS}$ , when  $K_3 \approx K_1$ , the four defects are confined at the thinnest part of the shell, as shown in Fig.2(a). This results from the non-uniform thickness of these experimental shells [13]. Due to the non-vanishing thickness of the shells, the  $+1/2$  defects are disclination lines that span the shell; to minimize their length, and thus the energy of the system, they group together at the thinner part of the shell. The approximate square arrangement of the defects comes from the approximate isotropy of the elastic constants at high temperatures. In fact, if  $K_3/K_1 = 1$ , the elastic energy associated with any director field is invariant under a  $\frac{\pi}{2}$  rotation in  $\mathbf{n}$ , converting bend distortions into splay distortions and vice versa. Therefore, the four defects must be located at the vertices of a square in their equilibrium configuration when  $K_3/K_1 = 1$ .

At intermediate temperatures, when  $1 < K_3/K_1 < \infty$ , the energy invariance under a  $\frac{\pi}{2}$  rotation of  $\mathbf{n}$  is broken, and thus, the four defects are necessarily arranged in a rhombus structure. Since  $K_1$  does not change much in the temperature range studied, the motion of the defects is mainly controlled by the energy term associated to bend. To explain why the distance between defects 1-2 becomes larger than the distance between defects 3-4 when  $K_3/K_1$  increases, we investigate how increasing  $K_3$  affects the equilibrium texture shown schematically in Fig.2(h), where  $K_3 \simeq K_1 \equiv K$ . This nematic texture has a free energy that depends on  $K$  and the core energies of the defects. Now, we consider an increase of

the bend constant from  $K$  to  $K_3 = K + \Delta K_3$ , while we keep the position of the defects fixed. The additional bend energy density,  $f_b$ , associated to this increase in the bend constant is mainly controlled by the radius of curvature of the director lines on the sphere. For a longitudinal director field such as the one shown in Fig.2(k),  $f_b$  is zero since the integral curves of the director field are great circles, whereas  $f_b = \Delta K_3 \cot^2 \theta / 2R^2$  for a latitudinal texture [14]. In Fig.2(h), the curvature of the director lines is given by the locations of the defects, which allow us to split the sphere into two caps. In the lower cap, defined by the position of defects 3 and 4 [shaded region in Fig2(h)], the magnitude of  $f_b$  is given by  $f_b^{(1)} \approx \Delta K_3 \cot^2(\alpha_{34}/2) / 2R^2$ , while for the remaining part of the sphere,  $f_b^{(2)} \approx \Delta K_3 \cot^2(\alpha_{12}/2) / 2R^2$ . The corresponding energies,  $F_b^{(1)}$  and  $F_b^{(2)}$ , can be respectively obtained as  $F_b^{(1)} = f_b^{(1)} V^{(1)}$  and  $F_b^{(2)} = f_b^{(2)} V^{(2)}$ , where  $V^{(1)}$  and  $V^{(2)}$  are the volumes corresponding to the regions considered. In spherical coordinates,  $V^{(1)} = \int_0^{\alpha_{34}/2} 2\pi R^2 h (1 - \cos \theta) \sin \theta d\theta \approx \pi R^2 h \alpha_{34}^4 / 64$  and  $V^{(2)} \approx 4\pi R^2 h$ . In the limit of small angular distances, we obtain  $F_b^{(1)} \approx \pi h \Delta K_3 \alpha_{34}^2 / 32$  and  $F_b^{(2)} \approx 8\pi h \Delta K_3 / \alpha_{12}^2$ . The motion of the defects must be driven by the relaxation of this additional bent energy. Since  $F_b^{(1)} \sim \alpha_{34}^2$  and  $F_b^{(2)} \sim \alpha_{12}^{-2}$ , the system will spontaneously increase  $\alpha_{12}$  as  $K_3$  increases, as we observe experimentally.

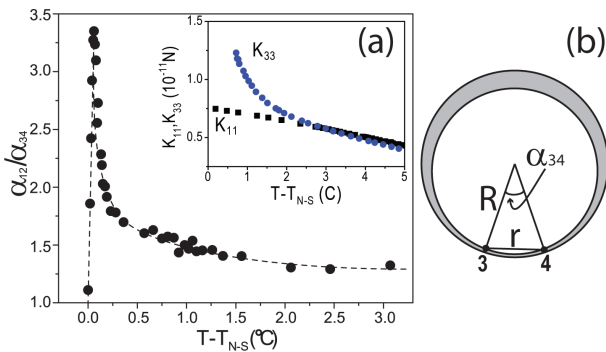


FIG. 3: (a) Ratio between the angular distances  $\alpha_{12}$  (between defects 1-2) and  $\alpha_{34}$  (between defects 3-4) as a function of  $T - T_{NS}$ . The inset shows the variation of  $K_3$  and  $K_1$  versus  $T - T_{NS}$  [11]. (b) Geometric definition of  $\alpha_{34}$ .

At  $T_{NS}$ , the shell becomes smectic. In the smectic phase, the molecules assemble in equispaced layers perpendicular to  $\mathbf{n}$ . From a geometric point of view, the nematic texture shown in Fig.2(k) can be readily converted into a simple smectic texture that preserves the four  $s = +\frac{1}{2}$  defects [15]. The resulting smectic texture is schematically represented in Fig.4(a),  $\mathbf{n}$  is aligned along great circles and the bi-dimensional layers follow latitude lines. Experimentally, however, the texture develops a series of additional distinctive patterns in time. Just after the phase transition, a set of longitudinal lines

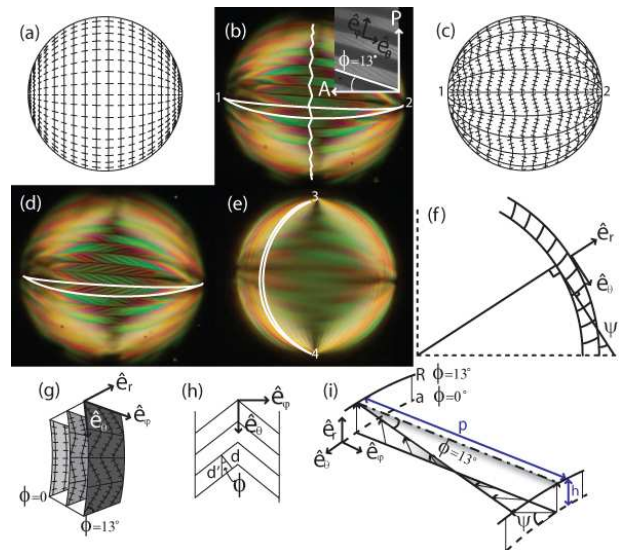


FIG. 4: (a) Longitudinal texture in a bi-dimensional smectic shell. The schematic shows the director field (discontinuous lines) and smectic layers (continuous lines) on the upper hemisphere. (b) Birefringence texture observed in experimental smectic shells, where curvature walls divide each hemisphere in crescent domains. The inset in (b) shows that  $\mathbf{n}$  is tilted in opposite directions in adjacent domains. (c) Director field corresponding to the texture shown in (b), where the walls provoke a zig-zag modulation of the smectic layers. (e) Secondary curvature walls provoking a secondary optical modulation inside crescent domains. (d) Primary curvature walls at the thinner part of the shell. (f) Local 3-dimensional smectic texture resulting from the bi-dimensional one shown in (a). (g) Possible 3-dimensional texture in which the smectic layers twist through the shell thickness. (h) In this configuration, the effective layer thickness  $d'$  increases at the outer sphere compensating the effect of the different curvatures of the inner and outer spheres. (i) This texture implies a large tilt angle  $\psi$  with respect to the outer sphere normal.

form on the thicker part of the shell along the direction of the former director field, as shown in Fig.4(b). These lines connect defects 1 and 2 and divide the shell into several crescent domains; one of those domains is highlighted in Fig.4(b). As the sample is rotated between cross-polarizers, the extinction angle periodically changes from  $-13^\circ$  to  $+13^\circ$  from one crescent domain to the next one, as shown in the inset of Fig.4(b). Since  $\mathbf{n}$  tilts in opposite symmetric directions in adjacent domains, the longitudinal lines can be identified as curvature walls [16]. We note that the resultant zig-zag modulation of the smectic layers reminds of the patterns observed after a Helfrich Hurault instability, as schematically indicated in Fig.4(c).

After formation of these curvature walls, we observe that a secondary set of curvature walls form, but these have a much smaller angular distortion,  $\approx 1^\circ$ , than the first. They extend across each domain perpendicularly to the tilted director field and give rise to a dark/light

striped pattern inside domains, as shown in Fig.4(d). The transition ends with the formation of primary curvature walls at the lower hemisphere, as shown in 4(e).

The description provided up to this point implicitly considers that  $\mathbf{n}$  is uniform through the shell thickness, which is equivalent to a concentric stacking of the bi-dimensional structure of Fig. 4(c). Within this picture, the curvatures walls would stem from the significant splay distortions in Fig. 4(a), which are released via the dilation of the layers at the walls [6]. Alternatively, the walls could result from the non-zero thickness of our experimental shells, as explained below.

In a thick shell, where the inner and outer spheres have significantly different radii, a strict planar anchoring can be satisfied on the inner sphere but not on the outer one; this results from the fact that having strong planar anchoring on a curved surface is only compatible with a bulk smectic texture without defects or layer dilations if the smectic layers grow outwardly from the convex side of the surface [15]. As a result, the smectic layers filling the shell are necessarily tilted at the outer surface violating the preferred planar anchoring and entailing an anchoring energy cost. To illustrate this, we construct a local bulk smectic texture from a surface texture with planar anchoring in Fig.4(f); the result is a tilt angle,  $\psi$ , at the outer surface. For typical  $R = 119\mu\text{m}$  and  $h = 4\mu\text{m}$ , we obtain a typical tilt angle  $\psi = \arccos(a/R) \approx 15^\circ$ .

It is tempting to think that this supplementary anchoring energy can be decreased if the smectic layer is progressively twisted from the inner sphere to the outer sphere in the way shown in Fig.4(g). The twist angle is  $\phi = 13^\circ$  at the outer sphere and  $\phi = 0$  at the inner sphere. Note that this twist implies a slight dilation of the layers via curvature walls. The zig-zag of the smectic layers at the surface sphere implies these are longer than the corresponding smectic layers at the inner sphere; this corresponds to a larger effective layer separation,  $d' = d/\cos\phi$ , with  $d$  is the spontaneous thickness of the layer [see Fig.4(h)]. The number of smectic layers on both surfaces is the same when  $d'/d = R/a$  or equivalently when  $\cos\phi = a/R$ . For typical values of  $R$  and  $a$ , we obtain a twist angle at the outer surface of  $\phi = 15^\circ$ , consistent with our experimental observations. Such an arrangement, however, also induces a tilt in the layers at the outer surface. Accommodating  $\phi = 0$  at the inner surface and  $\phi = 13^\circ$  at the outer surface without layer dilation entails tilting the smectic layer by an angle  $\psi$ , with maximal value given by  $\tan\psi = h/(p\tan\Phi)$ , where  $p$  is the width of the corresponding crescent domain [see Fig. 4(i)]. Using the experimental values  $p \approx 15\mu\text{m}$ ,  $\phi \approx 13^\circ$  and  $h \approx 4\mu\text{m}$ , we obtain  $\psi = 45^\circ$ , implying there is also an important penalty in anchoring energy in the case of the considered twisted structure. Detailed energy calculations are required in order to elucidate the

ultimate origin of the observed curvature walls.

Nematic shells undergo significant configurational changes as  $K_3/K_1$  is varied. When  $K_3/K_1 \approx 1$ , the four  $s = +\frac{1}{2}$  defects appear confined in the thinnest part of the shell, approximately located at the vertices of a square. By contrast, when  $K_3/K_1 \gg 1$ , the four defects relocate on the equatorial plane, confirming recent theoretical and simulation expectations [9, 10]. The transition between these two limiting configurations proceeds continuously through a series of equilibrium states in which the defects typically arrange in a rhombus whose diagonals ratio depends on the value of  $K_3/K_1$ . This offers new possibilities for controlling the position of defects, and eventually, if these are functionalized, the directionality of the interactions between shells. New types of defects, not observed in shells before, appear when the nematic order is replaced by smectic order. At this point, we observe the formation of primary and secondary curvature walls, whose origin we have discussed by considering two possible scenarios. Our results open the way to rigorous theoretical calculations and exemplify the richness of behaviors that can be obtained when the elasticity of the material or the degree of order in the shell is changed.

T.L-L. thanks the European Marie Curie Program (IEF-236091). A.F-N. thanks the National Science Foundation (DMR-0847304).

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\* Electronic address: [Teresa.Lopez-Leon@univ-montp2.fr](mailto:Teresa.Lopez-Leon@univ-montp2.fr)

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