Mechanically Induced Biaxial Transition in a Nanoconfined Nematic Liquid Crystal with a Topological Defect

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Using an atomic force microscopy, we have measured the separation dependence of the force between an atomically flat mica sheet and a micrometer-sized glass sphere immersed in the nematic liquid crystal. As the mica surface induces a strong parallel alignment and the treated glass sphere induces a strong perpendicular alignment on the liquid crystal, a repulsive force is observed due to the elastically deformed nematic liquid crystal. We observe that below a critical separation $d_{\mathrm{th}} \approx 10$ nm, the system undergoes a structural transition, thus relaxing the distortion. The results are interpreted within the eigenvalue exchange mechanism using the Landau–de Gennes tensorial approach.

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Nematic liquid crystals (NLC) are orientationally ordered fluids in which rodlike molecules are spontaneously aligned into a certain direction called the director $\vec{n}$. The degree of local orientation is characterized by a tensorial order parameter $\mathbf{Q}$ [1], where the eigenvectors of $\mathbf{Q}$ describe the preferred molecular orientations and the eigenvalues measure the degree of order in each direction. When the NLC is confined between two surfaces with competing boundary conditions, the director field is elastically distorted and the order parameter varies locally. The total free energy of the NLC depends on the surface separation, which results in structural forces between the confining surfaces.

Structural forces are responsible for many spectacular phenomena in nematic colloids, where fascinating and robust self-assembled colloidal structures were reported recently, such as 1D colloidal chains [2], 2D crystals [3], entangled colloidal wires [4], and others. Nematic colloids are not only interesting as a generic system for soft-matter physics, but they could also lead to novel materials for photonics, such as metamaterials [5]. The underlying concept, which is responsible for extreme robustness of nematic colloidal structures, is the sharing of elastically distorted regions around topological defects. These are remnants of the spontaneously broken symmetry of the isotropic phase and appear in the form of singular points or lines. Topological defects are ubiquitous in nature and are important in particle physics, cosmology, and condensed matter physics as well. They can be observed on a large scale in liquid crystals, which makes those a convenient generic system, where the topology of the tensor ordering field can be studied in great detail using optical microscopy. Whereas the nature of topological defects is well understood in micrometer-sized nematic colloids, their role in mediating surface forces at nanometer separation has remained largely unexplored [6].

In this Letter, we show that the behavior of topological defects in highly constrained nematic colloids is closely related to the *eigenvalue exchange problem* in a ''hybrid'' NLC layer with perpendicular alignment of NLC molecules on one surface and parallel alignment on the other, formulated by Palffy-Muhoray *et al.* [7]. Considering a hybrid cell, they have shown that for large thickness, the principal eigenvector (i.e., the nematic director) continuously rotates from the parallel to the perpendicular direction, moving from one interface to the other. Below a critical thickness, the system adopts the eigenvalue exchange configuration, where the eigenvectors remain fixed, while one of the eigenvalues continuously grows across the cell at the expense of the other, resulting in an intermediate thin biaxial transitional layer. A structural transition from the eigenvector rotation configuration to the eigenvalue exchange is expected when the confinement gap is decreased. Even though this structural transition has been attracting a tremendous attention of theory [8–12], it has only been observed indirectly during the electric-field-induced order reconstruction [13–15]. The difficulty is in imposing a well-controlled distortion of a NLC on a nanometer scale, which can be achieved very precisely by the atomic force microscopy (AFM) in the force spectroscopy mode [16–18].

Here we report experimental evidence of the eigenvalue exchange in a thin hybrid NLC layer in the presence of a topological defect, which is present due to the geometry of the experiment. Nematic liquid crystal 5CB (4-*n*-pentyl-4-cyanobiphenyl, Merck) is confined between a freshly cleaved mica sheet, inducing strong parallel alignment and a micrometer-sized glass sphere

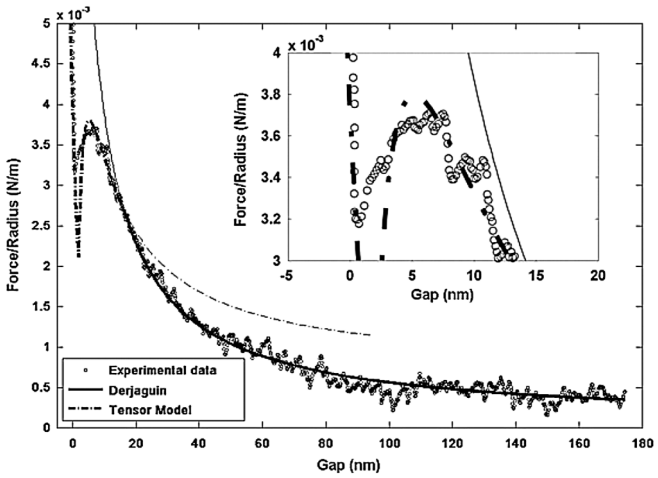

FIG. 1. Force (open circles) mediated by a thin hybrid 5CB nematic layer confined between a homeotropic sphere and a planar mica surface. The force is monotonically repulsive for $d > 15$ nm and follows the Frank-Derjaguin model (solid line). When $d \sim \xi_b$, the force becomes nonmonotonic but still repulsive and is described by the tensorial LdG model for a hybrid cell with defect (dashed line). In the inset, the small separation region is enlarged.

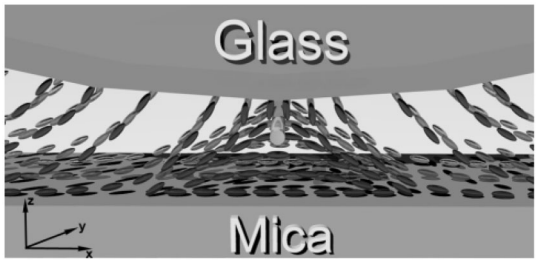

FIG. 2. Orientation of the molecules in a thin film of a nematic liquid crystal 5CB, which is confined between a DMOAP covered glass sphere and a flat mica surface. The alignment is planar on the flat mica surface and homeotropic on the curved surface of the sphere. The topological constraint creates a disclination line, passing through the contact point.

treated with DMOAP (*N, N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride) for strong perpendicular alignment. The force F, between the sphere, attached to the AFM cantilever, and the mica surface, is measured via the deflection of the cantilever [18]. At a critical separation of $\sim$10 nm, we observe a sudden decrease of the repulsive force. This is interpreted as squashing flat a topological defect into a biaxial layer, which is, in fact, the eigenvalue exchange and is well explained in terms of the Landau–de Gennes (LdG) theory [1].

A modified AFM head with a piezoresistive cantilever (elastic constant $k_l = 1$ N/m) was used for force detection [19], and the capillarity effects were avoided by immersing the sphere and the cantilever in the NLC [17,20]. The measured force on a sphere as a function of separation is shown in Fig. 1. As expected for an elastically deformed NLC, it is always repulsive and increases with decreasing separation, as the degree of the elastic deformation increases with decreasing separation. However, an interesting effect is observed when the separation is decreased below $\sim$10 nm: there is a sudden and noticeable decrease of the force below this thickness, which is a clear indication that the structure of the confined nematic has changed.

The orientation of molecules in a thin hybrid nematic layer is shown in Fig. 2. Because of topological constraints, a $-1/2$ disclination line appears [1], passing through the symmetry point. The core size of the disclination line is of the order of several nanometers; it sets the length scale and determines the interaction regimes. When the surface separation d is much larger than the defect core, a continuous elastic distortion of the director field $\vec{n}$ with constant order parameter, corresponding to the Frank elastic model, is considered, neglecting details close to the defect line. In this limit, the repulsive force for the hybrid geometry in the Derjaguin approximation [21] is $F = k\pi R\Delta\theta^2/d$, where k is an average elastic constant for director distortion, R is the radius of the sphere, d is the surface separation, and $\Delta\theta = \theta_p - \theta_h = \pi/2$, θ_p, and θ_h are the tilt angles with respect to the normal to each surface. The normalized force measured by the AFM is $F/R = \frac{k}{d+d_0}\frac{\pi^3}{4}$, where d_0 is the residual gap at the *hard contact*, which is not unusual in force experiments. For separation $d > 15$ nm, this equation perfectly describes the measured force, as shown by the solid line in Fig. 1. The parameters are $R = 9.7$ μm, which is close to $R_{\text{exp}} = (9.0 \pm 0.5)$ μm measured using an optical microscope, $k = 8$ pN and $d_0 = 5$ nm. The finite value of $d_0 = 5$ nm can be ascribed to additional molecular layers absorbed on the confining surfaces [16,17] and corresponds to a homeotropic monolayer of 5CB, adsorbed on the DMOAP [22], and a planar monolayer of 5CB, adsorbed on mica [23].

For shorter separations ($d < 15$ nm), the description of an elastically distorted director field obviously fails (see the solid line in Fig. 1). The measured force still remains repulsive but shows a sudden decrease that is not expected from the elastic model. On this scale, the gradient of the order and biaxiality become important and a tensorial representation of nematic order is required [1].

A rigorous treatment using the tensor formalism in the curved geometry is beyond the scope of this Letter. We simplify the plane-sphere geometry into the plane-plane hybrid geometry with a disclination line, which is justified at small separations ($d \ll R$). For a given surface separation d, the free energy $\mathcal{F} = \int(F_t + F_d)dV$ is calculated numerically using a finite element method and the force is the negative derivative of $\mathcal{F}$ with respect to d. F_t is the free energy density associated with the degree of nematic order, while F_d is the anisotropic elastic contribution to the free energy and accounts for any spatial gradients of $\mathbf{Q}$. The explicit form as well as a detailed description of the minimization procedure can be found in Ref. [12]. Since the system is translationally invariant along the disclina-

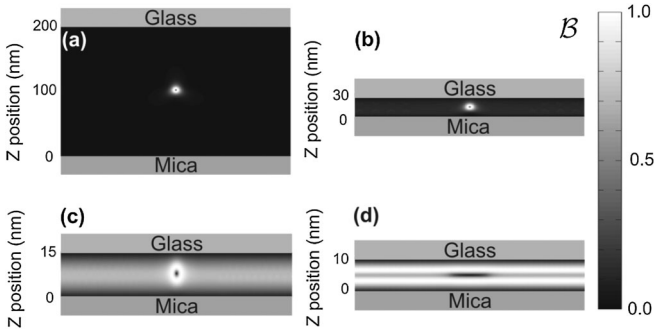

FIG. 3. Biaxiality $\mathcal{B}$ in a thin hybrid nematic layer with different thicknesses: (a) $d = 200$ nm, (b) $d = 30$ nm, (c) $d = 14$ nm, and (d) $d = 10$ nm. At large separation [(a) and (b)], the system is uniaxial everywhere except for a small region surrounding the defect core. As the gap is decreased, the defect core is deformed (c) and below some threshold gap d_{th} (d), the defect is expelled through the creation of a biaxial wall which connects the perpendicular and the parallel orientations. The lateral size is 300 nm.

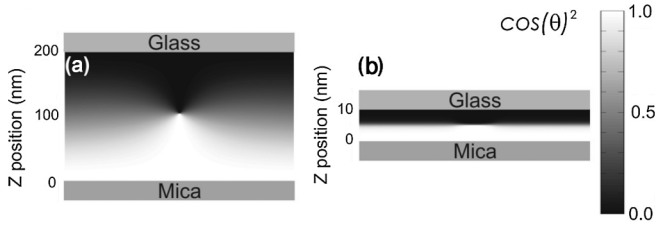

FIG. 4. Average molecular orientation described by $\cos(\theta)^2$ inside of the hybrid layer for (a) $d = 200$ nm and (b) $d = 10$ nm. θ is the angle between the average orientation of molecular long axis (i.e., the director) and the x direction.

tion line (y direction), the problem is two dimensional. The size of the system is $l = 800$ nm along the x axis, and in order to avoid the boundary effects, the force is calculated considering only the region $|x| < 100$ nm and $|y| < 100$ nm. The boundary conditions are rigid parallel on the plane at $z = 0$, rigid perpendicular on the plane $z = d$, and free on the planes $x = \pm l/2$. Therefore, the system has the shape of a rectangular cell surrounding the disclination line and is discretized in triangular elements. An adaptive mesh is used, which allows a finer discretization in the region of large $\nabla\mathbf{Q}$ as, for instance, around the defect.

Figure 3 shows the calculated biaxiality $\mathcal{B} = \sqrt{1 - 6[\text{tr}(\mathbf{Q}^3)]^2/[\text{tr}(\mathbf{Q}^2)]^3}$ [14] (which is a convenient parameter for illustrating spatial inhomogeneities of $\mathbf{Q}$) inside of the cell for different values of the cell gap d. At relatively large separations [Figs. 3(a) and 3(b)], the nematic is uniaxial everywhere ($\mathcal{B} = 0$) except for a small region around the defect core. Its size is a few biaxial coherence lengths $\xi_b = \sqrt{k/(S_{\text{bulk}}^3 b)}$ [24,25], where b is the cubic Landau coefficient, $S_{\text{bulk}} = 0.55$ and $\xi_b = 3.4$ nm, for 5CB at room temperature. When the gap d becomes comparable to ξ_b, the core of the defect *explodes* along the x direction and a large biaxiality propagates inside of the cell [Fig. 3(c)]. Further decrease of the confining gap results in the creation of a biaxial wall, connecting the two orthogonal uniaxial directions imposed by the boundary conditions. [Fig. 3(d)]. Even though a biaxial wall would also be created in the absence of a defect [9,12], the disclination line acts as a seed for the biaxiality here [25].

The dashed line in Fig. 1 is the force calculated within tensorial LdG model for a hybrid cell with a defect. For $d > 15$ nm, the force is monotonically decreasing with increasing d, the scalar order parameter S (which is the eigenvalue associated with the principal eigenvector of $\mathbf{Q}$ [1]) is constant, and the system is uniaxial everywhere except for a small region surrounding the defect [Figs. 3(a) and 3(b)]. For $d < 15$ nm, a nonzero biaxiality propagates inside of the system and S becomes inhomogeneous. The distortion concentrates in the regions of lower S, where the elastic constants, proportional to S^2, have lower values. The force reaches a maximum when d is comparable to the size of the biaxial ring surrounding the defect core (i.e., $d \sim 4\xi_b$). Here the confinement starts to stretch the defect structure along the x axis [Fig. 3(c)]. The force reaches a local minimum when the biaxial wall is fully developed (i.e., $d \sim 2\xi_b$). By comparing Figs. 3(a) and 3(d), we see that the system has transited from the *eigenvector rotation* into the *eigenvalue exchange* configuration by developing a thin transitional biaxial nematic layer, which originated from the biaxiality seed concentrated at the $-1/2$ defect.

Although our model employs rigid boundaries, we see from Fig. 1 that the agreement between the LdG theory and the experiment is good, even in the region below $d = 20$ nm. At this point, there are two questions that need to be addressed: (i) the validity of the LdG theory in NLC layers as thin as 20 nm and (ii) the validity of rigid boundary conditions and possible surface anchoring breaking [26] at such small separations. Question (i) has already been addressed and has been shown in numerous experiments that LdG theory provides correct quantitative prediction even when the distortion occurs on a length scale of a few molecular lengths [11–17,27]. Moreover, the predictions of LdG theory for strongly confined hybrid nematic films are in agreement with molecular dynamics [28] and Monte Carlo simulations [29,30]. We would also like to stress that the experimental force data in the inset to Fig. 1 are in good agreement with the force calculated from the tensorial LdG calculation below 10 nm, even though we were using a fixed set of LdG expansion coefficients determined for the bulk 5CB. This means that corrections of the mean-field theory due to fluctuations or finite-size effects are much smaller than the force resolution of our experiment.

As for question (ii), we know from AFM and surface force apparatus experiments that DMOAP coated glass and

mica surfaces show very high surface anchoring energies because of the presence of a first molecular layer strongly adsorbed on 5CB-DMOAP [22] and 5CB-mica interfaces [23]. This means that the surface anchoring breaking can occur only by *breaking the NLC itself* at the interface between these smecticlike first layers and the nematic bulk interior. However, recent developments show that the NLC can break only via biaxial melting [11–14,31], i.e., by creating a thin biaxial layer between the surface-adsorbed molecular layer and the interior of the nematic. This leads us to a very important conclusion: the explosion of the $-1/2$ defect into a thin biaxial layer at critical surface-surface separation is, in fact, the surface anchoring breaking. The biaxial layer mediates the transition from the first smecticlike layer of 5CB perpendicularly adsorbed to the DMOAP silanated glass surface and the crystal-like layer of 5CB molecules adsorbed on crystalline mica surface.

Figure 4 shows how the molecular orientation, described by $\cos(\theta)^2$, varies inside of the hybrid layer for (a) $d = 200$ nm and (b) $d = 10$ nm. Here, θ is the angle between the average orientation of the molecular long axis and the x direction. At large separation [Fig. 3(a)], θ varies smoothly everywhere except across the defect, which connects two orthogonal orientations by means of a biaxial core. At shorter separations [Fig. 3(b)], the variation of θ is discontinuous, and the planar orientation is abruptly transformed into the perpendicular one through a biaxial wall parallel to the confining surfaces.

Our experiment is also in agreement with measurements of elastic forces between a pair of micrometer-sized dipolar magnetic colloidal particles in NLC by Noel *et al.* [6]. By pressing colloids together, they observed a similar expulsion of a hedgehog point defect at a critical force of $F_{\mathrm{crit}}/R \approx 1.5$ mN/m, which is quite comparable to ours, $F_{\mathrm{crit}}/R \approx 3.5$ mN/m. However, colloidal experiments are far from being able to resolve the details of this process, which are clearly resolved in our AFM experiment. Therefore, these experiments all support our arguments that the measured force profile is the result of the eigenvalue exchange structural transition in a hybrid nematic under extreme confinement, which is, in fact, surface anchoring breaking initiated from a localized topological defect.

Let us conclude by noting that in spite of a simplified picture, the consistency of theory and experimental data is extremely satisfying, suggesting that our model captures the most relevant physical aspects. We conclude that below a threshold thickness of a hybrid nematic layer with a topological defect, an eigenvalue exchange transition occurs, and the defect is squashed flat into a biaxial layer. We show that for the surfaces used in our experiment, the surface anchoring of nematic molecules is so strong that the eigenvalue exchange is, in fact, playing the role of the surface anchoring breaking. We are confident that this result is important for future studies of topological defect-mediated interactions of submicron colloidal particles in nematics, where the conditions of extreme confinement of a complex fluid are expected.

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