Temperature-driven anchoring transitions at liquid crystal / water interfaces

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Abstract

Controlling the anchoring of liquid crystal molecules at an interface with a water solution influences the entire organization of the underlying liquid crystal phase, which is crucial for many applications. The simplest way to stabilize such interfaces is by fabricating single emulsions of liquid crystal in water; however, a greater sensitivity to interfacial effects can be achieved using double emulsions, i.e. liquid crystal shells. Anchoring transitions on those systems are traditionally triggered by the adsorption of surfactant molecules onto the interface, which is neither an instantaneous nor a reversible process. In this study, we report the ability to change the anchoring of 5CB, one of the most widely used liquid crystals, at the interface with dilute water solutions of PVA, a polymer surfactant commonly used for stabilizing liquid crystal shells. Anchoring transitions on those systems are traditionally triggered by the adsorption of surfactant molecules onto the interface, which is neither an instantaneous nor a reversible process. In this study, we report the ability to change the anchoring of 5CB, one of the most widely used liquid crystals, at the interface with dilute water solutions of PVA, a polymer surfactant commonly used for stabilizing liquid crystal shells, simply by controlling the temperature in the close vicinity of the liquid crystal clearing point. A quasi-static increase in temperature triggers an instantaneous change in the film’s boundary conditions from parallel to perpendicular, owing to the disordering effect of PVA, prior to the phase transition of the bulk 5CB. We study this anchoring transition on both flat suspended films and spherical shells of liquid crystals. Switching anchoring entails a series of structural transformations involving the formation of transient structures in which topological defects are stabilized. The type of defect structure depends on the topology of the film. This method has the unique ability to influence both interfaces of the film nearly at the same time, and can be applied to transform an initially polydisperse group of nematic shells into a monodisperse population of bivalent shells.

Introduction

Nematic liquid crystals are a fascinating class of soft matter systems. They combine the solid-like property of long-range orientational order with the fluid-like ability to reorganize under very weak external stimuli. Liquid crystal molecules exhibit preferential orientation at interfaces, a phenomenon called anchoring. These boundary conditions are transmitted to the bulk molecules via the elasticity of the liquid crystal. Therefore, by tuning the anchoring at the interfaces, one can influence the organization of the bulk of a liquid crystal sample. Hence control over anchoring is one of the most valuable tools for investigating the fundamental principles that govern the organization of liquid crystals systems. It also lies at the core of many applications, in particular in display technology, where liquid crystals are in contact with a solid substrate. Consequently, anchoring effects on a solid boundary have been extensively studied, and various techniques have been established to enforce specific molecular orientations at interfaces between liquid crystals and solids. These orientations are referred to as planar, when the molecules lie in the plane of...
the substrate; homeotropic, when they are perpendicular to it; or conical, when the angle that they make with the plane is between 0° and 90°.

Interfaces between liquid crystals and other unmiscible liquids, such as water, have recently attracted special attention. From a fundamental point of view, fluid interfaces have remarkable properties: being free from chemical or roughness defects, they are much more spatially homogeneous than solid boundaries. In terms of anchoring, they only prescribe the out-of-plane angular component of the preferred orientation: the in-plane component is degenerate, enabling the bulk liquid crystal a greater freedom of organization. In addition, they have recently shown great potential for building chemical or biological sensors. Indeed, microscopic events such as the adsorption of a protein at the liquid crystal / water interface can trigger a change in anchoring, which propagates a different orientation to the bulk molecules, in turn inducing a macroscopic change in the optical appearance of the sample. Most of these sensors take the form of flat nematic/water interfaces, however, some recent studies have shown the advantages of curved interfaces. They can be obtained by confining liquid crystals in capillaries or in droplets.

Nematic droplets are the simplest systems whose topology stabilizes defects in the liquid crystalline order – points where the director, i.e. a nonpolar vector field indicating the average molecular orientation at a mesoscopic scale, is undefined. An anchoring transition on a drop therefore translates to a modification of its topology, leading to a striking change between well-known optical patterns. Yet, the low surface-to-volume ratio of a droplet makes its behavior mostly governed by bulk effects. Finally, liquid crystal shells – spherical films of liquid crystal suspended in an aqueous solution – provide a system that combines the sensitivity to interfacial events of thin films with the stabilization of topological defects of droplets. Anchoring transitions in shells have been used as a means to induce topological transitions between various shell states, enabling the investigation of the fundamental nature of topological defects. While droplet-based liquid crystal sensors have been shown to be easier to read than their flat counterparts, anchoring transitions in shells have already been exploited for the detection of biochemicals in small concentrations.

The traditional method for inducing anchoring transitions at liquid crystal / water interfaces, whether in flat films, droplets, or shells, consists in dissolving surfactant molecules in the water phase. Commonly used liquid crystals such as cyanobiphenyls display planar anchoring when in contact with water. The adsorption of surfactants onto the interface typically forces the liquid crystal molecules to reorient in the direction of the surfactant alkyl chains, therefore inducing homeotropic anchoring. This method comes with several shortcomings. Firstly, one cannot switch instantaneously and reversibly between anchoring states within the same system. Indeed, the dynamics of the transition is governed by surfactant adsorption, which may not be uniform throughout the interface, and whose temporal evolution cannot be controlled accurately. Secondly, one cannot induce an anchoring transition on both interfaces of a shell at the same time, as the outer interface is the only one accessible to the surfactants. Indeed, although these molecules can diffuse through a liquid crystal membrane, it typically takes them about a day to do so, dissociating the anchoring transition on the inner interface from the one on the outer interface.

In this article, we report a new method to induce anchoring transitions at liquid crystal / water interfaces that addresses those issues. Interestingly, it relies on polyvinyl alcohol (PVA), a polymer surfactant widely used for stabilizing double emulsions. We show that it displays a temperature-dependent influence on anchoring. We focus on the interface between water solutions of PVA and 4-cyano-4′-pentylbiphenyl (5CB), one of the most widely used liquid crystals. We demonstrate that the usual planar anchoring prescribed by the contact between water and 5CB at room temperature is replaced by homeotropic anchoring when the temperature is brought just a few tenths of degrees Celsius below the clearing point of the liquid crys-
tal. This anchoring transition is nearly instantaneous, as well as spatially homogeneous, and affects simultaneously all the interfaces of the liquid crystal. We study the transition in both spherical nematic shells and flat suspended nematic films. The latter provides a new experimental platform extremely sensitive to interfacial phenomena. In both cases, the change of boundary conditions triggers a series of structural transformations in the system, imposing the formation of topological defects with integer topological charge. The number of defects and their organization depends on the geometry of the film.

**Materials and methods**

In this paper, we study anchoring transitions in suspended nematic films, which are thin nematic films sandwiched between two aqueous phases. We consider two different geometries: flat and spherical nematic films. Producing a spherical nematic shell is the simplest way to stabilize a liquid crystal film in water without the assistance of any solid boundary. While surface tension tends to preserve the spherical geometry of shells, it makes flat films unstable. For this reason, producing flat suspended nematic films is experimentally difficult. Here we propose a strategy to stabilize such films.

The commonly used method for stabilizing water / liquid crystal interfaces was developed by Abbott and coworkers. It relies on the use of a transmission electron microscopy (TEM) grid, a small metal disk 3.05 mm in diameter and 18 µm in thickness, having an array of holes with a given geometric shape. The grid is placed on top of a glass substrate, so that the pores of the grid become micro-sized observation cells. Confining the liquid crystal to these cells prevents it from dewetting the water interface by pinning it to a solid substrate. When the cells are immersed in an aqueous solution, the liquid crystal is sandwiched between a fluid and a solid interface. The glass solid substrate is usually coated with octadecyltrichlorosilane (OTS) in order to provide a very strong homeotropic anchoring. These anchoring cues on the bottom interface constrain the system, reducing its sensitivity to subtle anchoring changes occurring at the free interface.

To produce a free-standing film in water, in which the anchoring at the two interfaces is controlled by the aqueous solution, we used double "oyster" grids consisting of two laterally-fused standard grids. Fig. A shows one of these grids (inset) and the observation chamber in which they were placed. The 500 µm high cylindrical observation chamber was built by stacking ten layers of double-sided tape (Gudy 804, Filmolux) on a glass slide. A double oyster grid (GD50/100-Cu, Gilder) was deposited on the tape, in such a way that one of the single grids was stuck to the tape while the second one was suspended in mid-air. Ten more layers of tape were added on top of the first ones, bringing the overall thickness of the chamber to one millimeter. 0.1 µL of 5CB (Synthon Chemicals) or 6CB (Sigma-Aldrich) were deposited on the grid. The observation chamber was then filled with the aqueous phase, which could either be pure deionized water (Millipore Synergy), or a PVA solution (13-23 kg · mol⁻¹, Sigma-Aldrich). Filling the chamber also removed the excess of liquid crystal on the grid. The chamber was finally sealed with a glass cover slip. For observation, we focused on a single square hole in the grid.

Nematic shells of 5CB were produced using a glass capillary device. Briefly, a water / liquid crystal compound jet is sheared by a water-based outer solution using a combination of co-flow and flow-focusing geometries, and breaks up into double emulsions, as shown in Fig. C. To reach production regimes at reasonable flow rates, the viscosity of the outer phase was increased by adding 60 % wt glycerol (VWR Chemicals). The inner phase was either pure deionized water or a 1 % wt PVA solution. The shells were collected in a 200 µm high cylindrical observation chamber built by stacking two layers of double-sided tape. The continuous collection phase was identical to the inner phase, with traces of glycerol originating from the outer phase in the capillary device. Due to a slight density difference between 5CB and the water phases, the inner water droplet...
Figure 1: Films and shells of nematic liquid crystals in water. In this study, two complementary experimental systems were used: thin nematic films (top row) and nematic shells (bottom row). A) Nematic films were produced by fixing a copper double TEM grid in mid-height of an observation chamber filled with a water solution. One half of the double grid was embedded into the walls of the chamber, made of double-sided tape, while the other single grid was filled with a sub-microliter volume of liquid crystal. B) Cross-section of a cell of the grid filled with liquid crystal. The cell is 430 µm in width, 18 µm in thickness. The film is about 5 µm in the center. The vertical scale has been exaggerated ten times with respect to the horizontal scale. C) Nematic shells were produced by using a microfluidic device made of two tapered glass capillaries facing opposite directions, nested in a larger square capillary (not shown). D) Cross-section of a nematic shell. The thickness is heterogeneous due to a slight difference in density between the water phases and the 5CB. The typical outer diameter is 100 µm while the typical mean thickness is 10 µm.

Results and discussion

Temperature-driven anchoring transitions in nematic films

As widely reported, 5CB displays planar anchoring when in contact with an aqueous solution containing PVA. This is consistent with the strong birefringence colors displayed by our suspended nematic films at room temperature, as shown in Fig. 2A-i, which is a cross-polarised image of a 5CB film suspended in a 0.1% wt PVA solution. The colors become more and more vivid towards the center of the cell, indicating that the film is concave. Using a Michel-Levy chart, we estimate that its thickness ranges from 10 µm on the edges to 5 µm in the center. Since the contact with the metallic sub-
Figure 2: 5CB film in a 0.1 % wt PVA solution undergoing a slow temperature ramp
Top: series of top-view micrographs through crossed polarizers. Bottom: series of cross-sections schematically depicting the molecular arrangement at the location of the white rectangle. Throughout, the film is 430 µm wide, about 10 µm thick close to the edges, about 5 µm thick in the center, and is attached to a suspended copper TEM grid. The film undergoes a temperature ramp with a rate of 0.01 °C · min⁻¹. i) In most of the nematic range, the film displays strong birefringence colors, an indication of the planar anchoring that aligns the molecules parallel to the interfaces. ii) A few tenths of degrees Celsius below the phase transition temperature of pure 5CB, the interfacial mixture of PVA and 5CB molecules becomes isotropic. This induces an anchoring transition from planar to homeotropic at the interface with the bulk pure 5CB. iii) When the temperature gets even closer to the phase transition of pure 5CB, flattened droplets of isotropic phase nucleate at the top and bottom interfaces of the film, inducing conical anchoring of the remaining nematic pure 5CB in the bulk, in the form of apparent "birefringent islands". iv) The isotropic islands grow in size until the whole film turns isotropic.
of the microscope (Fig. 2B-ii). The bright rim corresponds to the region where the director transitions to accommodate the homeotropic anchoring cues on the edges of the grid with the homeotropic anchoring cues on the top and bottom interfaces. We were able to maintain the film in this state for more than eight hours by keeping the temperature constant.

The perpendicular orientation of the liquid crystal molecules was confirmed by studying 5CB films doped with an anisotropic fluorescent dye. We used the anisotropic dye N,N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP), which aligns with the 5CB molecules. The intensity of the fluorescence signal is minimum when the dye molecules are oriented along the direction of light propagation. When imaging the transition from the birefringence colors to the dark state, we observed that the fluorescence in the homeotropic region was indeed less intense than in the planar region, as shown in Supplementary Fig. 7. Also as expected, the isotropic state at the end of the evolution of the film showed intermediate intensities, about two-thirds of the way from homeotropic to planar levels.

For a temperature even closer to the clearing point, the film enters a state of coexistence between the nematic and isotropic phases, revealed by the formation of a myriad of birefringent islands (Fig. 2A-iii). When temperature is increased from the homeotropic state, an isotropic domain nucleates from the grid walls towards the center of the film at the expense of the homeotropic domain, which progressively shrinks. The most striking feature of this transition is the reappearance of birefringence in the form of a number of bright disk-like islands embedded in the homeotropic region, studied in detail in Fig. 3. This transition is hysteretic since cooling down an isotropic film at the same rate does not produce these islands: the front separating the isotropic from the homeotropic nematic phase progresses until the homeotropic phase just disappears.

The structure of the islands can be revealed by investigating their properties, both static and dynamic (Fig. 3, Supplementary Movie 1 and Supplementary Fig. 8). They stem from the nucleation of flattened droplets of isotropic phase at the liquid crystal / water interface. These isotropic pancakes enforce conical anchoring to the surrounding nematic liquid crystal explaining the re-emergence of birefringence. In bright field, all islands exhibit a point defect at their center and a sharp boundary with the surrounding homeotropic domain (Fig. 3A). Under crossed polarizers, they display first-order blue-gray interference colors, meaning that the liquid crystal region contributing to the birefringence is very thin (Fig. 3B). The defects are located at the intersection of four dark brushes which follow both polarizers when rotated, indicating that their topological charge is [+1]. When a first-order retardation plate is added, the liquid crystal molecules are found to be arranged radially from the defect (Fig. 3C). The absence of [+1/2] defects – which induce a π-rotation of the director, and thus, are only allowed when the boundary conditions are planar – is consistent with the existence of conical anchoring cues at the boundaries.

Monitoring the evolution of the islands in time reveals additional information about their nature. The islands nucleate in the homeotropic domain. As temperature rises, they slowly grow in diameter, their color remaining unchanged. Then they meet one of two possible outcomes, or a combination of both. On the one hand, they can disappear by coalescence: two islands fuse from the side, creating a [-1] defect at the junction, which quickly annihilates with one of the [+1] defects from the original islands (Supplementary Fig. 8A). Yet islands can sometimes be seen to overlap without coalescing. In these instances, the interference colors add up but the geometry of the patterns remains unperturbed (Supplementary Fig. 8B). This demonstrates that the islands lie at the liquid crystal / water interfaces: in most experimental realizations, they only form at either the bottom or the top interface, but sometimes they appear on both, in which case they can only interact with islands on the same interface. On the other hand, they can collide with the boundary between the homeotropic domain and the isotropic phase. In this case,
Figure 3: Flattened isotropic droplets embedded into a homeotropic nematic domain in a 5CB film close to the clearing point. A) Bright field (single polarizer). From the edges to the center of the cell, one can make out the isotropic domain, the homeotropic nematic domain, and the circular islands with their central point defect. B) Crossed polarizers. The [+1] charge of all defects is revealed. First-order birefringence colors indicate that only a small thickness of liquid crystal has tilted back towards the planes of the interfaces. C) Crossed polarizers with first-order retardation plate. The radial orientation of the long axis of the molecules is revealed. Throughout, the film is 430µm wide. D) Schematic of a typical isotropic droplet, top and side view.

they fuse with the isotropic phase (Supplementary Fig. 8A). We confirmed the nature of these islands by observing the phase transition of a thin nematic film (approximately 30µm thick) confined between two glass plates treated to induce strong homeotropic anchoring (see Supplementary Information and Supplementary Movie 2). Finally, we note that the same islands were reported by Abbott et al. very recently, and that their analysis is consistent with ours.

**Anchoring transition mechanism**

We hypothesized that the anchoring transition was induced by the PVA. Since the PVA chains lie at the liquid crystal / water interface (Fig. 2A-i), they disrupt the nematic arrangement of the liquid crystal molecules close to the interface. Therefore, the order parameter of the nematic phase is expected to be lower near the interface than in the bulk. With greater disorder comes a lower phase transition temperature: hence, the interfacial mixture of PVA chains and 5CB molecules has a slightly lower clearing point than the pure 5CB bulk. This suggests that the anchoring transition corresponds to an interfacial melting of the PVA-5CB mixture, which in turn induces a homeotropic anchoring of the pure 5CB bulk.

We were able to confirm that the PVA was triggering the anchoring transitions by performing a new set of experiments in pure water, which did not yield any anchoring transitions. Films went directly from planar nematic to isotropic, as can be seen in Supplementary Movie 3 and Fig. 4A. This is a standard phase transition, not accompanied by an anchoring transition. Upon repeating the experiment with PVA solutions with various concentrations, we established that 0.1% wt was the minimum value that leads to an anchoring transition.

We were also able to prove that the anchoring transition temperature was indeed linked to the liquid crystal, by conducting additional experiments with a different liquid crystal of the same series. While the clearing point of 5CB is around 34.5°C, 4-cyano-4′-hexylbiphenyl (6CB) has a phase transition temperature at around 29.5°C. Performing the same experiments with 6CB yielded identical results, albeit uniformly shifted in temperature: an anchoring transition was observed a few tenths of degrees Celsius below the clearing point when the liquid crystal was in contact with a 0.1% wt PVA solution; no anchoring transition was observed prior to the phase transition when in contact with pure water.

**Application to nematic shells**

This new mechanism, characterized in thin nematic films, can be profitably applied in liq-
Figure 4: 5CB film and shell in pure water solutions undergoing a slow temperature ramp. As temperature of a film (A) or a shell (B) is increased, the nematic phase is progressively replaced by the isotropic phase, without any significant change in the shrinking planar texture. Throughout both experiments, the temperature ramp has a rate of 0.01°C·min⁻¹. The film is 430 µm wide and the shell is about 200 µm in outer diameter.

By varying the composition of the water phases, we were able to selectively trigger the anchoring transition on shells. Liquid crystal shells are usually stabilized by adding PVA to the aqueous phase; however, those shells can be also produced without adding any stabilizer. While regular water-in-oil-in-water double emulsion destabilizes in a matter of seconds without a surfactant, this is not the case when the middle phase is a liquid crystal, since rupturing the shell would trigger the nucleation of additional topological defects. This process has a large energy barrier associated to it, which stabilizes the double emulsion. For this reason, we were able to produce 5CB shells with pure water as the inner and outer solutions. These shells were subjected to a 0.01°C·min⁻¹ temperature ramp, as shown in Supplementary Movie 4 and Fig. 4B. We witnessed the nucleation and growth of the isotropic phase within the planar nematic phase, until it took over the whole shell, the planar texture remaining unchanged throughout the entire process.

However, when the shells were produced with 1% wt PVA in water as the inner and outer solutions, under the same experimental conditions, two anchoring transitions occurred ahead...
Figure 5: **5CB shell in a 1% wt PVA solution undergoing a slow temperature ramp** Top: micrographs of a shell under crossed polarizers. Bottom: cross-section of the shell schematically depicting the molecular arrangement. Throughout, the shell is 110 µm in outer diameter and has a 15 µm average thickness. The temperature ramp has a rate of 0.01 °C·min⁻¹. i) For most of the nematic state, the shell displays three defects, indicating that molecules within the shell are oriented parallel to the interfaces. ii) A few tenths of degrees Celsius below the phase transition temperature of the bulk 5CB, the shell transitions to a structure having only two [+1] defects, only one of them being visible here. This is a signature of hybrid anchoring, where the molecules have planar anchoring on one interface and homeotropic anchoring on the other. iii) Even closer to the phase transition temperature, the shell displays a classic Maltese cross, which shows that the anchoring has switched to being perpendicular on both interfaces. iv) In the end, the entire shell turns isotropic.

of the phase transition, as depicted in Supplementary Movie 5 and Fig. 5. As the temperature slowly rose, three states could be unambiguously identified – a planar state (Fig. 5-i), a hybrid state (Fig. 5-ii), and a homeotropic state (Fig. 5-iii) – before the shell turned isotropic (Fig. 5-iv). The planar state is the one that was discussed above; the boundary conditions are planar at both interfaces. The hybrid state corresponds to a situation where the anchoring cues are planar at one interface and perpendicular at the other one. As the director has to adapt smoothly to these conflicting boundary conditions, it is necessarily tilted in the bulk. In this situation, half-integer defects are no longer allowed: while the orientation of rod-like molecules lying in a plane is unchanged by a π rotation, this is no longer the case when the molecules acquire polarity by tilting out of the plane. For this reason, hybrid shells can only display surface defects with integer topological charge. Since topological defects are not required on the surface with homeotropic anchoring, hybrid shells are necessarily bivalent, the two defects being diametrically opposed to one another, as they only feel the inter-defect repulsion. These structural features, along with a characteristic vividly-colored and twisted texture, enable one to recognize hybrid shells under the microscope. Similarly, the homeotropic state corresponds to shells having matching homeotropic boundary conditions at both interfaces; such shells are defect-free, with a uniform, radially-oriented director. Their optical signature is a series of colored rings barred with a large Maltese cross. It is in fact the same pattern obtained by illuminating a flat nematic cell with a uniform, vertically-oriented director in convergent light – known as a uniaxial conoscopic interference figure.

On the one hand, there is no coexistence state between the isotropic and the nematic phase: the islands from the flat film were not observed. We hypothesize that a solid boundary is manu-
tory for forming the islands. On the other hand, the presence of the hybrid state was unexpected; we hypothesize that the convex and concave natures of the outer and inner interfaces, respectively, play a role in delaying the interfacial melting of the 5CB/PVA mixture at one of the boundaries. Yet it enabled our new technique to be used with a new goal in mind.

Hence, we finally showed that this method could be exploited to control the valency of a population of shells. Typically, shells are produced in an out-of-equilibrium fashion, often yielding a polydisperse population – i.e. composed of shells with various metastable defect configurations, or valencies – such as depicted in Fig. 6A. This particular collection of shells was subjected to a 0.01°C·min⁻¹ temperature ramp: the shells went through all of the previously described states, until all of them turned isotropic. The sample was then cooled down with a −0.01°C·min⁻¹ temperature ramp. The shells went through all of the states again, this time in reversed order, until the planar texture was retrieved. However, at this stage, all of the shells had the same defect configuration, as seen in Fig. 6B. This evolution can additionally be witnessed in Supplementary Movie 6.

Instead of exhibiting the lowest-energy configuration, with four [+1/2] defects, they displayed a higher-energy configuration, with two [+1] defects. Indeed, our study shows that the phase transition is accompanied by an anchoring transition, which alters the topological constraints on the shell. As the hybrid state forbids the presence of half-integer defects, the shell is topologically prevented from reaching its equilibrium state. Therefore, our method turns an initially polydisperse shell population into a monodisperse population of bivalent shells.

Conclusion
We have established a new temperature-driven method for inducing an anchoring transition from planar to homeotropic, which is immediate, spatially homogeneous, and can affect both interfaces of a film. It is achieved with a precise control over the temperature of a 5CB/water interface in the vicinity of its clearing point. We observed that the anchoring transition took place if PVA was dissolved in the water in concentrations greater than 0.1% in weight. We explain this behavior by the melting of the disordered PVA/5CB mixture at the interfaces of the shell, which occurs at a lower critical temperature than that of pure 5CB. The presence of a new isotropic interfacial layer induces homeotropic anchoring of the underlying pure nematic 5CB. We find that the two interfaces in a nematic shell are not affected at exactly the same temperature; this yields a hybrid transitional state that can be used to transform an initially polydisperse population of shells, i.e. displaying all possible defect configurations, into a monodisperse population of bivalent shells.

This work raises a number of new questions beyond its scope, which would constitute an interesting follow-up. In particular, quantitative measurements of the anchoring strength and precise imaging of the director throughout the bulk of the film at various stages of the transition would be of great interest. Our study expands the number of available parameters one can play with to induce dynamical transitions in shells of more complex liquid crystal phases.

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Figure 6: **Controlling shell valency by going through the hybrid state** i) Group of polydisperse nematic shells, i.e. displaying all three possible planar defect configurations. ii) Same group of nematic shells, showing only bivalent configurations after being subjected to a 0.01 °C/ min temperature ramp up to the isotropic phase, then to a −0.01 °C/ min temperature ramp back to the planar phase. Residual flow within the observation cell shifted the shells’ position during the temperature ramps.

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**Supporting Information Available**

The following files are available free of charge.
Temperature ramp on a homeotropic 5CB cell with solid boundaries

A small drop of 5CB was deposited between two glass slides treated with OTS so as to impose a strong perpendicular alignment of the molecules. Under crossed polarizers, a uniformly dark area was selected, and the sample was submitted to a 0.01 °C·min⁻¹ temperature ramp. In the nematic state, conoscopy yielded a Maltese cross characteristic of homeotropic anchoring. A few tenths of degrees Celsius below the clearing point, we witnessed the rise of birefringence colors, signalling the presence of the isotropic/nematic interface. The colors and the way they nucleated were very reminiscent of our isotropic islands. However, while the island were nicely rounded by surface tension in the case of an all-liquid system, they were of a very irregular shape in the homeotropic cell, probably due to pinning on surface defects. Then fully black patches started appearing where the isotropic phase had reached both walls of the cell, until they took over the entire cell. This experiment in a more well-known situation validates the weakly out-of-plane nature of the anchoring 5CB and its isotropic phase.

Supplementary figures

Supplementary movies

- SupMov1_HeatingFilmPVA: timelapse of the temperature-driven anchoring transition of a 5CB film in a 0.1% PVA solution in water, corresponding to Fig. 2.

- SupMov2_HeatingHomeoCell: timelapse of a 5CB homeotropic cell heated quasi-statically in the vicinity of its clearing point.

- SupMov3_HeatingFilmPureWater: timelapse of the phase transition of a 5CB film in a solution with less than 0.1% PVA in water, corresponding to Fig. 4A.

- SupMov4_HeatingShellPureWater: real-time movie of the phase transition of a 5CB shell without PVA in the inner and outer water phases, corresponding to Fig. 4B.

- SupMov5_HeatingShellPVA: timelapse of the temperature-driven anchoring transition of typical 5CB shells, with 1% PVA in the outer and inner phases, corresponding to Fig. 5.

- SupMov6_HeatingCoolingShellsPVA: timelapse of the temperature-driven anchoring transitions of typical 5CB shells with 1% PVA in the water phases as the sample is heated to isotropic then cooled back to nematic, corresponding to Fig. 6.

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Figure 7: **5CB films doped with BTBP in a 0.1 % wt PVA solution undergoing a slow temperature ramp** Left: micrographs between crossed polarizers, lit under both white light and near-ultraviolet light. Right: micrographs in fluorescence mode (single polarizer), lit under near-ultraviolet light. Bottom: average intensity profiles in a 25-pixel wide band along the SW-NE diagonal of the films. The U-shape of all the graphs is due to the concavity of the film: there is more material on the edges, hence more dopant, on the edges than in the center. Throughout, the films are 430 µm wide, about 10 µm thick close to the edges, about 5 µm thick in the center, and fixed on a suspended copper TEM grid. The temperature ramp has a rate of 0.01°C · min⁻¹. The series of pictures depicts typical stages of the evolution of a film, as temperature is increased: i) planar state (blue curve), ii) transition from the planar to the homeotropic state (yellow curve), iii) homeotropic state (red curve), iv) early stage with the birefringent islands, v) late stage with the birefringent islands (purple curve), vi) almost all of the film has turned isotropic (green curve). The transition between planar and homeotropic levels shows a clear jump in fluorescence intensity. The isotropic profile shows intermediate values, about two thirds of the way between planar and homeotropic levels. The corners appear very dark due to remaining patches of homeotropic nematic phase. The late island stage profile shows a similar behavior as the isotropic profile; the peak on the left part corresponds to a birefringent island.
Figure 8: **Additional clues pertaining to the isotropic islands** Micrographs showing isotropic islands on a 5CB film in a 0.1% wt PVA solution in water, scale bars 50 µm. A) Coalescence of islands and merging into the isotropic phase. Time series as the temperature is linearly increased with a 0.01 °C · min⁻¹ temperature ramp. Two isotropic islands are initially apart (i), they coalesce, creating an $s = -1$ defect at the neck of the junction (ii-iii). The new defect then annihilates with one of the two $s = +1$ initial defects (iv-v). Lastly, the remaining island fuses with the isotropic phase, growing from the right side of the image (vi-viii). B) Overlapping islands. Pictures in bright field, crossed polarizers, and crossed polarizers with first-order retardation plate. The temperature is a few tenths of degrees Celsius below the clearing point of pure 5CB. One island is located on one of the two interfaces of the film, while the other three islands are located on the second interface.
Graphical TOC Entry

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