



HAL
open science

Temperature-Driven Anchoring Transitions at Liquid Crystal/Water Interfaces

Guillaume Durey, Yoko Ishii, T. Lopez-Leon

► **To cite this version:**

Guillaume Durey, Yoko Ishii, T. Lopez-Leon. Temperature-Driven Anchoring Transitions at Liquid Crystal/Water Interfaces. *Langmuir*, 2020, 36 (32), pp.9368-9376. <10.1021/acs.langmuir.0c00985>. <hal-03063570>

HAL Id: hal-03063570

<https://hal.science/hal-03063570v1>

Submitted on 8 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Temperature-driven anchoring transitions at liquid crystal / water interfaces

Guillaume Durey, Yoko Ishii, and Teresa Lopez-Leon

Langmuir, **Just Accepted Manuscript** • DOI: 10.1021/acs.langmuir.0c00985 • Publication Date (Web): 21 Jul 2020

Downloaded from pubs.acs.org on August 4, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Temperature-driven anchoring transitions at liquid crystal / water interfaces

Guillaume Durey,^{†,¶} Yoko Ishii,[‡] and Teresa Lopez-Leon^{*,†}

[†]*Laboratoire Gulliver, UMR CNRS 7083, ESPCI Paris, Université PSL, 10 rue Vauquelin, 75005 Paris, France*

[‡]*Department of Physics, Graduate School of Science, Kyoto University, Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto, 606-8562, Japan*

[¶]*School of Engineering, Brown University, 184 Hope Street, Providence, RI 02912, USA*

E-mail: teresa.lopez-leon@espci.fr

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 droplets of liquid crystal in water; however, a greater sensitivity to interfacial effects can be achieved using liquid crystal shells, i.e. spherical films of liquid crystal suspended in water. 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 4-cyano-4'-pentylbiphenyl (5CB), one of the most widely used liquid crystals, at the interface with dilute water solutions of polyvinyl alcohol (PVA), a polymer 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 reorientation of the molecules from parallel to perpendicular to the interfaces, owing to the local disordering effect of PVA on 5CB, 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 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 technologies, where liquid crystals are in con-

1 tact with a solid substrate. Consequently, anchoring effects on a solid boundary have been
2 extensively studied.^{1,2} Two parameters govern
3 the anchoring of a liquid crystal: the preferred
4 molecular orientation at the interface (known
5 as the easy axis) and the energetic penalty as-
6 sociated to violating this orientation (known as
7 the anchoring strength). One speaks of planar
8 anchoring when the easy axis lies in the plane
9 of the substrate; homeotropic anchoring when
10 it is perpendicular to it; or conical anchoring
11 when the angle is between 0° and 90° .

12 Interfaces between liquid crystals and other
13 immiscible liquids, such as water, have recently
14 attracted special attention. From a fundamen-
15 tal point of view, fluid interfaces have remark-
16 able properties: being free from chemical or
17 roughness defects, they are much more spa-
18 tially homogeneous than solid boundaries. In
19 terms of anchoring, they only prescribe the
20 out-of-plane angular component of the pre-
21 ferred orientation: the in-plane component is
22 degenerate, enabling the bulk liquid crystal a
23 greater freedom of organization. In addition,
24 they have recently shown great potential for
25 building chemical or biological sensors.³⁻⁵ In-
26 deed, microscopic events such as the adsorp-
27 tion of a protein at the liquid crystal / wa-
28 ter interface can trigger a change in anchoring,
29 which propagates a different orientation to the
30 bulk molecules, in turn inducing a macroscopic
31 change in the optical appearance of the sample.
32 Most of these sensors take the form of flat ne-
33 matic/water interfaces;^{6,7} however, some recent
34 studies have shown the advantages of curved
35 interfaces. They can be obtained by confining
36 liquid crystals in capillaries,^{8,9} droplets,¹⁰⁻¹² or
37 spherical shells.¹³

38 Nematic droplets are the simplest systems
39 whose topology stabilizes defects in the liq-
40 uid crystalline order – points where the di-
41 rector, i.e. a nonpolar vector indicating the
42 average molecular orientation at a mesoscopic
43 scale, is undefined.^{14,15} An anchoring transi-
44 tion on a drop therefore translates to a mod-
45 ification of its topological constraints, leading
46 to a striking change between well-known opti-
47 cal patterns. Yet, the low surface-to-volume
48 ratio of a droplet makes its behavior mostly

governed by bulk effects. Finally, liquid crys-
tal shells – spherical films of liquid crystal
suspended in an aqueous solution – provide
a system that combines the sensitivity to in-
terfacial events of thin films with the stabi-
lization of topological defects of droplets.¹⁵⁻¹⁸
The study of anchoring transitions in shells
has a fundamental interest besides the de-
velopment of applications. The two inter-
faces confining the shell allow for four different
types of boundary conditions: planar-planar,
planar-homeotropic, homeotropic-planar and
homeotropic-homeotropic. Switching from one
type of boundary condition to another usually
triggers dynamical transitions involving the for-
mation and recombination of topological de-
fects.¹⁹⁻²⁴ Transitions from purely planar or
homeotropic states to hybrid states have been
used to obtain information about the funda-
mental nature of topological defects,^{19,22} and
to make them interact in unusual ways.²⁰ In
contrast, direct transitions between purely pla-
nar and purely homeotropic states remain elu-
sive when using traditional methods to control
the orientation of the liquid crystal molecules
at fluid interfaces.

The traditional method for inducing anchor-
ing transitions at liquid crystal / water inter-
faces, whether in flat films,²⁵ droplets,^{26,27} or
shells^{13,19-22,24,28} consists in dissolving surfac-
tant molecules in the water phase. Commonly
used liquid crystals such as cyanobiphenyls dis-
play planar anchoring when in contact with
water. The adsorption of surfactants onto
the interface typically forces the liquid crys-
tal molecules to reorient in the direction of
the surfactant alkyl chains, therefore inducing
homeotropic anchoring. This method comes
with several shortcomings, especially when con-
sidering transitions on shells. Firstly, one can-
not switch instantaneously between anchoring
states in a controlled way. Indeed, the dy-
namics of the transition is governed by sur-
factant adsorption, whose spatiotemporal evo-
lution cannot be controlled accurately. Sec-
ondly, the switching process is not reversible.
While adding surfactants to the continuous
phase without altering the shell position is
tricky, flushing the shell with water to remove

1 the surfactants without losing it is impracti-
2 cable. Thirdly, one cannot induce an anchor-
3 ing transition on both interfaces of a shell at
4 the same time, as the outer interface is the
5 only one where the concentration of surfactants
6 can be tuned directly. Indeed, although these
7 molecules can diffuse through the liquid crys-
8 tal film, from the continuous aqueous phase
9 to the inner water droplet, it typically takes
10 them about a day to do so – leaving the shell
11 with ill-defined boundary conditions for an ex-
12 tended period of time. Despite recent efforts to
13 induce controlled anchoring transitions in liq-
14 uid crystal shells,^{24,29} a powerful alternative to
15 traditional surfactant-induced techniques is still
16 missing.

17
18
19 In this article, we report a new method to in-
20 duce a change in boundary conditions at liquid
21 crystal / water interfaces that addresses those
22 issues. It relies on coating the interface with
23 polyvinyl alcohol (PVA), a polymer widely used
24 for stabilizing double emulsions and for enforc-
25 ing strong planar anchoring. We show that
26 PVA enables a richer control over the molec-
27 ular anchoring at a fluid interface than what
28 was previously thought: it is actually possible
29 to tune its influence on the underlying liquid
30 crystal phase through a precise control of the
31 temperature of the system. We focus on the in-
32 terface between water solutions of PVA and 4-
33 cyano-4'-pentylbiphenyl (5CB), one of the most
34 widely used liquid crystals. We demonstrate
35 that the usual planar alignment at room tem-
36 perature is replaced by perpendicular align-
37 ment to the interfaces when the temperature
38 is brought just a few tenths of degrees Cel-
39 sius below the clearing point of the liquid crys-
40 tal. With this easily controllable experimen-
41 tal parameter, one can therefore have the sys-
42 tem switch between two antagonist anchoring
43 states. This anchoring transition is nearly in-
44 stantaneous, as well as spatially homogeneous,
45 and affects nearly simultaneously all the in-
46 terfaces of the liquid crystal. We first study
47 the transition in flat suspended nematic films,
48 which provide a new experimental platform ex-
49 tremely sensitive to interfacial phenomena. We
50 then demonstrate its usefulness by applying it
51 on liquid crystal shells, in which the change of

boundary conditions triggers a series of struc-
tural transformations, imposing the formation
of topological defects with integer topological
charge.

Materials and methods

For this study, we consider two different ge-
ometries: spherical nematic shells and flat sus-
pended nematic films. Shells provide a simple
way to stabilize a liquid crystal film in water
without the assistance of any solid boundary.
While surface tension tends to preserve such a
spherical geometry, it makes flat films unsta-
ble. Flat suspended films are more challenging
to stabilize, but provide a simpler geometry to
interpret anchoring transitions in a straightfor-
ward way, since curvature and topological con-
straints are not present. It thus constitutes a
good starting point for our study. Here we pro-
pose a strategy to stabilize such films.

A commonly used method for stabilizing wa-
ter / liquid crystal interfaces, developed by Ab-
bott and coworkers,²⁵ relies on confining the
liquid crystal to a transmission electron mi-
croscopy (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. In Abbott's system, 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 pre-
vents 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 enforce homeotropic anchoring. These
strong anchoring cues on the bottom interface
constrain the system, reducing its sensitivity to
subtle anchoring changes occurring at the free
interface.

Here, we propose a novel adaptation of Ab-
bott's system, which addresses those issues. In-
deed, we produced suspended films in water,
in which the anchoring at the two interfaces
is solely controlled by the aqueous solution.

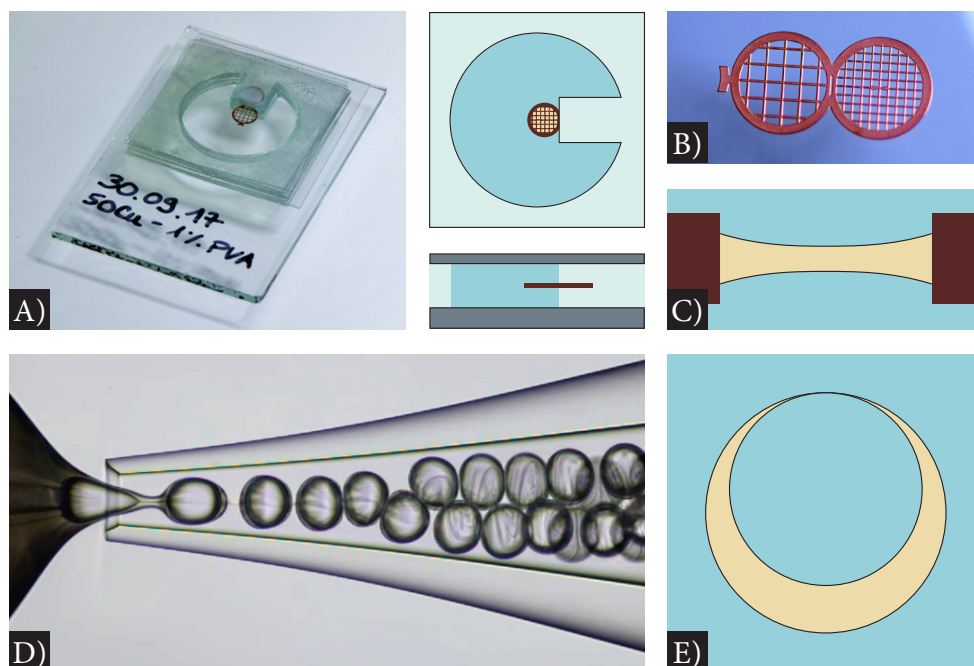


Figure 1: **Films and shells of nematic liquid crystals in water.** In this study, two complementary experimental systems were used: thin nematic films (top row) and nematic shells (bottom row). Nematic films were produced by fixing a copper double TEM grid in mid-height of an observation chamber filled 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. A) Photograph (left) and schematic representations (top right: top view, bottom right: side view) of the experimental chamber mounted on a microscope glass slide. B) Close-up photograph of a double TEM grid. Each grid is 3.05 mm in diameter. C) 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. Nematic shells were produced by using a microfluidic device made of two tapered glass capillaries facing opposite directions, nested in a larger square capillary. D) Microphotograph of shell production. The tip of the capillary is about 150 μm wide. E) Schematic representation of a vertical 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 .

To do this, we used double "oyster" grids,³⁰ consisting of two laterally-fused standard TEM grids. Fig. 1A shows the observation chamber in which they were placed, and Fig. 1B one of these grids. A 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 suspended grid in the middle plane of the one-millimeter-

high chamber. 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 $\text{kg} \cdot \text{mol}^{-1}$, 87-89% hydrolyzed, Sigma-Aldrich). Filling the chamber also detached an excess of liquid crystal from overfilled cells of the grid, generating a few microdroplets which adsorbed to the hydrophobic walls of the chamber. The chamber was finally sealed with a glass cover slip. For observation, we focused on a single square hole in the grid, a vertical cross-section of which is

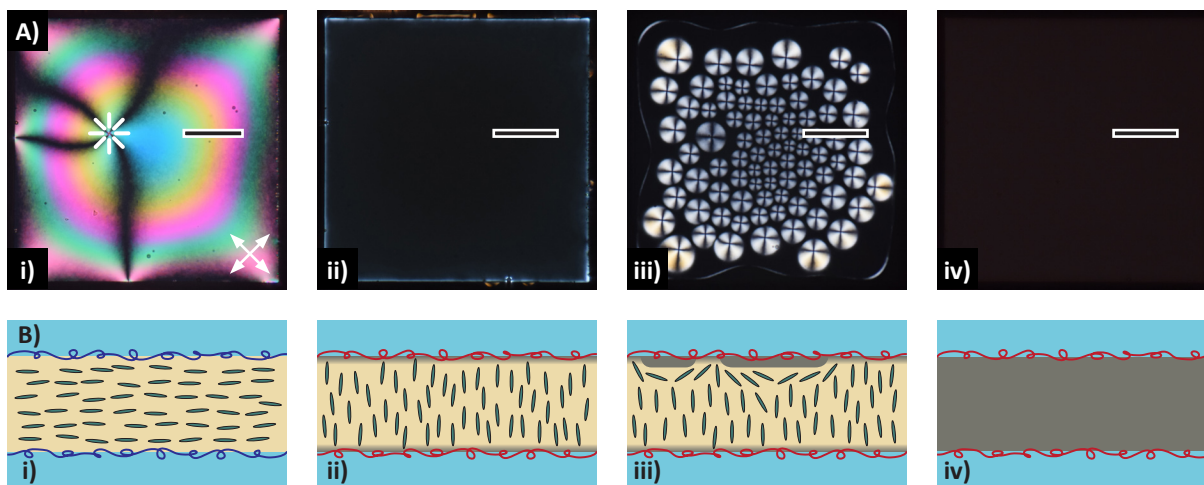


Figure 2: **5CB film in a 0.1 % wt PVA solution undergoing a slow temperature ramp** Top: series of top-view micrographs through crossed polarizers. Bottom: series of vertical cross-sections schematically depicting the molecular arrangement at the location of the black and white rectangle. Throughout, the film is $430\ \mu\text{m}$ wide, about $10\ \mu\text{m}$ thick close to the edges, about $5\ \mu\text{m}$ thick in the center, and is attached to a suspended copper TEM grid. The film undergoes a temperature ramp with a rate of $0.01\ ^\circ\text{C} \cdot \text{min}^{-1}$. 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. This particular film includes a topological defect; director field lines are sketched in its vicinity. The vertical cross-section is taken far from the defect, along a direction where the director is in the plane of the cross-section and uniform in this initial stage. ii) A few tenths of degrees Celsius below the phase transition temperature of pure 5CB, a molecular reorientation perpendicularly to the interfaces occurs, evidenced by a dark film with bright edges, likely due to the interfacial PVA-5CB mixture becoming isotropic. iii) When the temperature reaches the clearing point of pure 5CB, islands of bulk isotropic phase nucleate from the top and bottom interfaces of the film, inducing conical anchoring of the remaining nematic pure 5CB in the bulk. iv) The isotropic islands grow in size until the whole film turns isotropic. These four micrographs, taken respectively at $-0.05\ ^\circ\text{C}$, $-0.01\ ^\circ\text{C}$, $0.02\ ^\circ\text{C}$ and $0.11\ ^\circ\text{C}$ of the apparition of the first island of bulk isotropic phase, are frames of the timelapse provided in Supplementary Movie 1.

sketched in Fig. 1C.

Nematic shells of 5CB were produced using a glass capillary device.³¹ In this type of device, 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. 1C. To reach production regimes at reasonable flow rates, the viscosity of the outer aqueous phase was increased by adding 60 % wt glycerol (VWR Chemicals). The inner aqueous phase was either pure deionized water or a 1 % wt PVA solution. The shells were collected in a $200\ \mu\text{m}$ high cylindrical observation chamber built by stacking two layers of double-sided tape. The continuous collection phase was iden-

tical to the inner aqueous phase, with traces of glycerol originating from the outer aqueous phase in the capillary device. Due to a slight density difference between 5CB and the aqueous phases, the inner aqueous droplet typically rises to the top of the shell, making the shell heterogeneous in thickness.

We achieved an extremely fine level of temperature control in order to witness temperature-driven anchoring transitions on these experimental systems. The observation chambers were inserted into a TS62 thermal stage driven by a mK1000 unit, both from Instec. They were subjected to a $0.01\ ^\circ\text{C} \cdot \text{min}^{-1}$ temperature ramp close to the clearing point of the liquid crystal (around $34.5\ ^\circ\text{C}$ for 5CB,

around 29.5 °C for 6CB). Temperature was controlled with an accuracy better than a tenth of degree Celsius. The sample's evolution was recorded using a Nikon DSLR camera (D5300 or D300s) mounted on an upright polarized optical microscope (Nikon Ni-U).

Results and discussion

Temperature-driven anchoring transitions in nematic films

Parallel state

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. 2-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-Lévy chart,³² we estimate that its thickness ranges from 10 μm on the edges to 5 μm in the center. Besides, since the contact with the metallic substrate provides homeotropic anchoring,⁴ the liquid crystal molecules are arranged perpendicularly to the edges of the film and parallel to the interfaces with water, yielding a radial defect in the center of the cell in the specific case of the film featured in Fig. 2. Defects can be characterized by their topological charge, which quantifies the number of times the director rotates around the singularity. The defect in our film has a $[+1]$ topological charge, indicating a 2π -rotation of the director around the defect core. This can be distinguished by the number of dark brushes stemming from the defect, which is equal to four times the absolute value of its topological charge.

Interestingly, we observe that the molecular anchoring at the interfaces with the aqueous solution can be changed by accurately controlling the film temperature in the vicinity of its clearing point. By quasi-statically increasing the temperature of the system with a linear rate of $0.01\text{ }^\circ\text{C} \cdot \text{min}^{-1}$, we were able to sweep sequen-

tially through a series of distinct states with different boundary conditions until the entire sample turns isotropic. This evolution, recorded in Supplementary Movie 1, is as follows: the usual parallel state (Fig. 2-i), a new perpendicular state (Fig. 2-ii) and a coexistence state (Fig. 2-iii), before the isotropic state (Fig. 2-iv).

Perpendicular state

A few tenths of degrees Celsius below the phase transition temperature of the bulk 5CB, an unexpected abrupt reorientation to a perpendicular state occurs. Indeed, the appearance of the cell changes abruptly to a black film with a bright rim (Fig. 2-ii), a pattern which is recognized as the signature of homeotropic anchoring at a liquid crystal / water interface.²⁵ The loss of birefringence is explained by the reorientation of the long axis of the molecules in the bulk perpendicularly to the interfaces: the optic axis of the liquid crystal becomes aligned with the optical axis of the microscope. 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.³³ 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 Fig. S1. Also as expected, the isotropic state at the end of the evolution of the film went back up to intermediate intensities, about two-thirds of the way from homeotropic to planar levels. We considered the fluorescence emission as be-

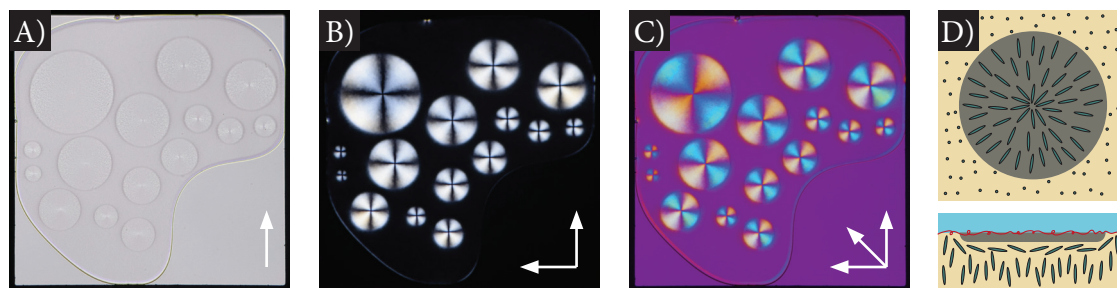


Figure 3: **Coexistence of regions of pure isotropic phase embedded into a homeotropic nematic domain in the bulk of a 5CB film, close to the clearing point.** A) Bright field (single polarizer). From the edges to the center of the cell, one can make out the isotropic domain, the homeotropic nematic 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 $430\ \mu\text{m}$ wide. D) Schematic of a typical isotropic droplet, top and side view.

ing temperature-independent over such a small temperature interval. Besides, if the temperature were to influence the fluorescence intensity, we would expect a continuous decrease. Yet we report non-monotonic behavior.

Coexistence state

For a temperature even closer to the clearing point, the film enters a state of coexistence between the bulk nematic and isotropic phases. When the temperature is increased from the perpendicular state, the isotropic phase nucleates from the grid walls, creating a homeotropically-aligned nematic domain no longer in contact with the walls, as shown in Fig. 2-iii. The most striking feature of this state is the reappearance of birefringence in the form of a number of bright disk-like islands embedded in the homeotropic region, introduced in Fig. 2-iii and studied in detail in Fig. 3. As the isotropic phase grows, the homeotropic domain shrinks – in Fig. 3, the homeotropic domain has shrunk more than in Fig. 2-iii. It eventually breaks up into multiple smaller domains, before the whole film turns isotropic. When the temperature is lowered from the isotropic state, at the same rate of $-0.01\ \text{°C} \cdot \text{min}^{-1}$, homeotropically-aligned domains of nematic phase nucleate from the isotropic phase, then merge and grow until the

whole film is homeotropic. Contrary to what happens upon heating the film, there are no birefringent islands formed at the coexistence state when the film is cooled.

The structure of the islands can be revealed by investigating their properties, both static and dynamic (Fig. 3, Supplementary Movie 1 and Fig. S2). They stem from the nucleation of flattened regions of isotropic phase at the liquid crystal / water interface, extending into the bulk of the nematic phase. This situation, where pure isotropic 5CB coexists with pure nematic 5CB, has been described in the literature.^{34,35} The isotropic phase of 5CB was reported to enforce out-of-plane anchoring of its nematic phase, at an angle of $26.5^\circ \pm 6^\circ$ from the surface.³⁴ This explains the re-emergence of birefringence around the islands of isotropic 5CB. 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

1 crystal molecules are found to be arranged radially from the defect (Fig. 3C). The absence
2 of $[+1/2]$ defects – which induce a π -rotation of
3 the director, and thus, are only allowed when
4 the boundary conditions are planar – is con-
5 sistent with the existence of conical anchoring
6 cues at the boundaries.^{36,37}

7
8 Monitoring the evolution of the islands in
9 time reveals additional information about
10 their nature. The islands nucleate in the
11 homeotropic domain. As temperature rises,
12 they slowly grow in diameter, their color re-
13 maining unchanged. Then they meet one of
14 two possible outcomes, or a combination of
15 both. On the one hand, they can disappear
16 by coalescence: two islands fuse from the side,
17 creating a $[-1]$ defect at the junction, which
18 quickly annihilates with one of the $[+1]$ defects
19 from the original islands (Fig. S2A). Yet islands
20 can sometimes be seen to overlap without co-
21 alescing. In these instances, the interference
22 colors add up but the geometry of the patterns
23 remains unperturbed (Fig. S2B). This demon-
24 strates that while the islands are located within
25 the bulk of the sample, they do not extend far
26 from the liquid crystal / water interfaces in
27 terms of depth. In most experimental realiza-
28 tions, they only form at either the bottom or
29 the top interface, but sometimes they appear
30 on both, in which case they can only interact
31 with islands on the same interface. On the
32 other hand, they can collide with the bound-
33 ary between the homeotropic domain and the
34 isotropic phase. In this case, they fuse with
35 the isotropic phase (Fig. S2A). We were able to
36 trigger the formation of identical islands in a
37 thin nematic film (approximately 30 μm thick)
38 confined between two glass plates treated to in-
39 duce strong homeotropic anchoring undergoing
40 a phase transition (see Supplementary Infor-
41 mation and Supplementary Movie 2). This
42 confirmed that their presence was indicative of
43 a simple phase coexistence in the bulk between
44 pure nematic and isotropic 5CB. Finally, we
45 note that the same type of islands were re-
46 ported by Abbott et al. very recently,³⁷ and
47 that their analysis is consistent with ours.
48
49
50
51
52
53
54
55
56
57
58
59
60

The role of PVA: experimental clues and mechanistic insights

Upon repeating these experiments for PVA so-
lutions with decreasing concentrations, we were
able to bring out the fact that a PVA concen-
tration above a certain threshold was a nec-
essary requirement for the temperature-driven
anchoring transition to take place. Indeed, no
anchoring transitions can be observed for sam-
ples with PVA below 0.1% wt in the aqueous
solution. Films go directly from planar nematic
to isotropic, as can be seen in Supplementary
Movie 3 and Fig. 4A, where the aqueous solu-
tion is simply pure water.

We were also able to prove that the value
of the anchoring transition temperature was
linked to the liquid crystal – not to the PVA
– by conducting additional experiments with a
different liquid crystal of the same series. While
the clearing point of 5CB is around 34.5 $^{\circ}\text{C}$, 4-
cyano-4'-hexylbiphenyl (6CB) has a phase tran-
sition temperature at around 29.5 $^{\circ}\text{C}$. Perform-
ing the same experiments with 6CB yielded
identical results, albeit uniformly shifted in
temperature: an anchoring transition was ob-
served 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 wa-
ter.

In the rest of this subsection, we offer sugges-
tions into the nature of the mechanism at play
in our experiments, although a conclusive ex-
perimental validation is out of the scope of the
present paper.

From the experiments mentioned above, it
seems that the temperature-induced anchor-
ing transition observed in the presence of PVA
stems from a change of interfacial order in the
film. Since the PVA chains lie at the liquid crys-
tal / water interface, they disrupt the nematic
arrangement of the liquid crystal molecules in
the vicinity. 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 tem-
perature: hence, such an interfacial mixture of

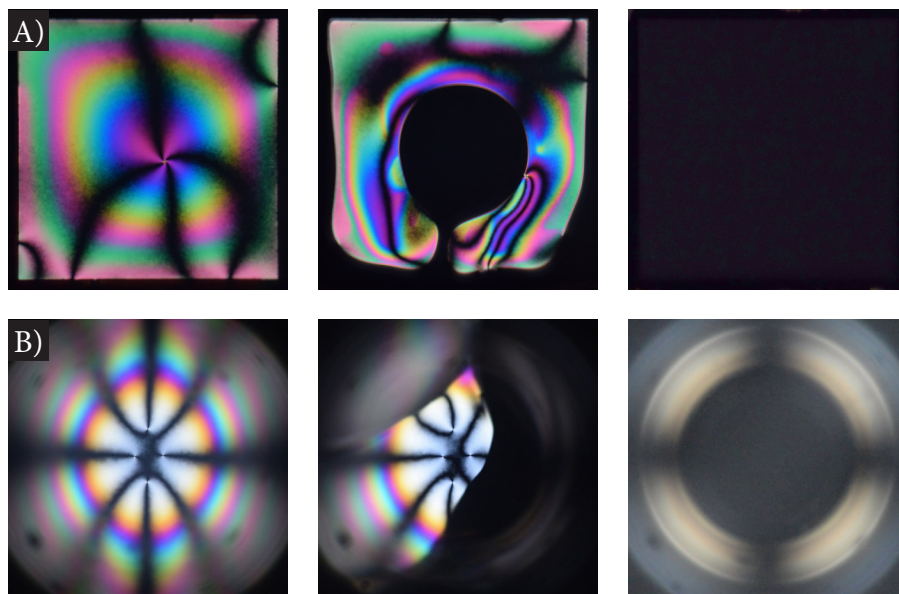


Figure 4: **5CB film and shell in pure water solutions undergoing a slow temperature ramp** As temperature of a film (A) or a shell (B) is increased, the nematic phase is progressively replaced by the isotropic phase, without any significant change in the shrinking planar texture. Throughout both experiments, the temperature ramp has a rate of $0.01\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The film is $430\text{ }\mu\text{m}$ wide and the shell is about $200\text{ }\mu\text{m}$ in outer diameter. The first series of micrographs corresponds to frames of the timelapse provided in Supplementary Movie 3, and the second series to frames of the real-time film provided in Supplementary Movie 4.

PVA chains and 5CB molecules would have a slightly lower clearing point than the pure 5CB bulk. This suggests that our system undergoes an interfacial melting of the PVA-5CB mixture before the bulk pure 5CB turns isotropic. Thus, we hypothesize that once this interfacial layer melts, a new interface appears in our films: it separates the isotropic PVA-5CB surface layer from the bulk nematic phase of pure 5CB. Such a localized phase transition in the presence of adsorbates has been reported in recent studies.^{37,38}

How does the presumed existence of this new interface cause the reorientation of the underlying liquid crystal molecules? The most probable hypothesis is that it induces a change in the easy axis accompanied by a decrease in anchoring strength. Indeed, it seems reasonable to think that the easy axis prescribed by the isotropic PVA-5CB surface layer is close to the one reported in the literature in the case of pure isotropic 5CB,^{34,35} thus imposing out-of-plane anchoring to the underlying bulk nematic film. Such boundary conditions would generate splay

and bend distortions of the director field in the nematic phase. Yet, as the anchoring strength between the nematic and isotropic phases of a single compound is relatively weak, it may be energetically favorable for the system to relax these distortions immediately, through the uniform reorientation of the molecules perpendicularly to the interfaces, violating the new easy axis in the process. A similar mechanism has been used to explain recent experimental findings.^{29,37,38} However, as far as we know, the easy axis at the interface of a bulk nematic phase with an isotropic PVA/5CB mixture has not yet been measured. An alternative possibility to the indirect mechanism above would be that the interfacial layer directly enforces homeotropic anchoring. Quantitative in-depth experiments are required to tell the two mechanisms apart.

Application to nematic shells

This new mechanism, characterized in thin nematic films, can be profitably applied in liquid crystal shells, altering the topological con-

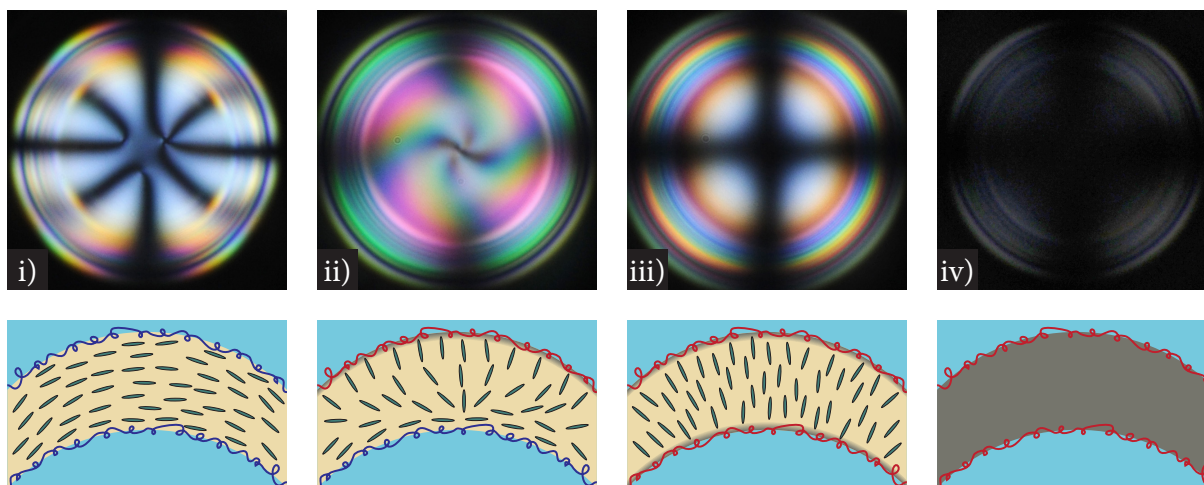


Figure 5: **5CB shell in a 1% wt PVA solution undergoing a slow temperature ramp** Top: micrographs of a shell under crossed polarizers. Bottom: cross-section of the shell schematically depicting the molecular arrangement. Throughout, the shell is $110\ \mu\text{m}$ in outer diameter and has a $15\ \mu\text{m}$ average thickness. The temperature ramp has a rate of $0.01\ ^\circ\text{C} \cdot \text{min}^{-1}$. 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. These four micrographs, taken respectively at $-0.43\ ^\circ\text{C}$, $-0.18\ ^\circ\text{C}$, $-0.03\ ^\circ\text{C}$ and $0.05\ ^\circ\text{C}$ of the first apparition of bulk isotropic phase, are close-ups of frames of the timelapse shown in Supplementary Movie 5.

straints they are subjected to. Shells were prepared with planar anchoring at both of their interfaces. As exemplified by the lines of latitude or longitude on a globe, nematic ordering under planar anchoring is frustrated on a sphere, and has to incorporate topologically-protected defects in the director. As a consequence of the Poincaré-Hopf theorem,^{39,40} the topological charges of the defects on such a sphere have to add up to $[+2]$. In nematics, topological charges higher than $[+1]$ are unstable, and pairs of defects with opposite topological charges annihilate. Therefore, planar nematic shells can either be bivalent ($2 \times [+1]$), trivalent ($1 \times [+1] + 2 \times [+1/2]$) or tetravalent ($4 \times [+1/2]$). Yet a three-dimensional shell is not a two-dimensional sphere: the defects are not surface points but disclination lines (singular or escaped) that span the shell thickness. Their equilibrium positions result from

the balance between the repulsion of positively-charged defects and the tendency of the lines to minimize their length by migrating to the region where the shell is thinner.¹⁶

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 a 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.¹⁴ 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 $0.01\ ^\circ\text{C} \cdot \text{min}^{-1}$ 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 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 radial 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 non-planar at the other one. Topological defects are not required on the surface if it has homeotropic anchoring. As the director has to adapt smoothly to the conflicting planar boundary condition on the other surface, 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, and are necessarily bivalent. The two defects are 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.^{19,20} Lastly, in the radial state, 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.¹⁵

These results show that temperature-driven anchoring transitions enable the rapid trans-

formation between shell states with matching anchoring at both interfaces. This is a clear improvement from traditional surfactant-driven anchoring transitions, which are limited to transformations between planar to hybrid or hybrid to homeotropic shell states. On the other hand, while in suspended films the anchoring transition occurred simultaneously at the top and bottom interfaces, this is no longer the case in shells: the transition at the inner interface is slightly delayed compared to the one at the outer interface, leading to stable hybrid shells. This last result was unexpected: we hypothesize that the convex and concave natures of the outer and inner interfaces, respectively, play a role in shifting the interfacial melting temperature of the 5CB/PVA mixture. Additionally, another difference between those two systems is the absence of a stable coexistence state between the isotropic and the nematic phase: the islands from the flat films were not observed in shells.

This new result enabled our new technique to be used with a new goal in mind: controlling 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. 6-i. This particular collection of shells was subjected to a $0.01\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ 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 $-0.01\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ 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. 6-ii. This evolution can additionally be witnessed in Supplementary Movie 6.

Instead of exhibiting the lowest-energy configuration, with four $[+1/2]$ defects,⁴¹⁻⁴³ 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

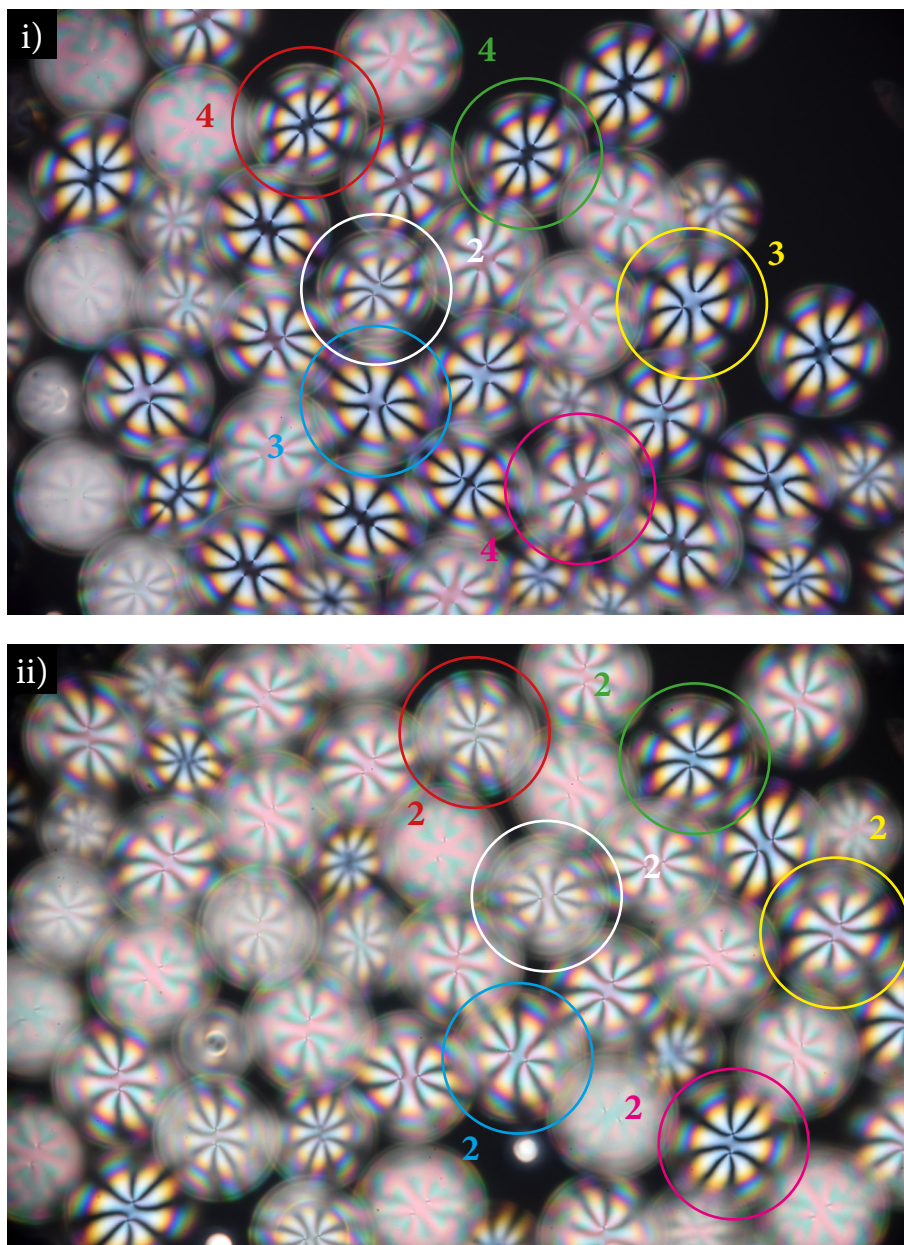


Figure 6: **Controlling shell valency by going through the hybrid state** i) Group of polydisperse nematic shells, i.e. displaying all three possible planar defect configurations. ii) Same group of nematic shells, showing only bivalent configurations after being subjected to a $0.01\text{ }^{\circ}\text{C}/\text{min}$ temperature ramp up to the isotropic phase, then to a $-0.01\text{ }^{\circ}\text{C}/\text{min}$ temperature ramp back to the planar phase. Residual flow within the observation cell shifted the shells' position during the temperature ramps. Those two micrographs are frames of the timelapse provided in Supplementary Movie 6.

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. This new ability to uniformize the defect configurations of a population of planar shells could prove very useful in the perspective of shell self-assembly through defect functionalization – a long-term goal which has motivated the experimental investigation of nematic shells since the very beginning.⁴⁴

Temperature-induced anchoring transitions in shells have been the object of a growing interest in the past few years.^{21,22,24,29} In particular, we note that in,²¹ Lagerwall et al. performed a similar experiment on planar shells of 5CB, dispersed in 1% wt PVA in a 50:50 volume ratio water/glycerol mixture. However, no anchoring transition was reported when the shells were subjected to a 0.01 °C/min temperature ramp. We were able to attribute experimentally the difference in behavior compared to our results to the large concentration of glycerol in the water phases, which is known to affect the surface activity of surfactant molecules.

Conclusion

We report a temperature-driven method for inducing molecular reorientation in a liquid crystal film, which is immediate, spatially homogeneous, and can affect both interfaces of the film. It is achieved with a precise control over the temperature of an aqueous interface of 5CB in the vicinity of its clearing point. The anchoring transition takes place if PVA is dissolved in 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 this new isotropic interfacial PVA-5CB mixture could be responsible for the reorientation of the underlying pure nematic 5CB. This new method allows us to control the boundary conditions of the most widely researched shell system, shells of 5CB in aqueous solutions of PVA, without changing the compo-

sition of the system, just by using an external stimulus. It remarkably enables rapid transformations between planar and radial shell states. We find that the two interfaces in a nematic shell are not affected at exactly the same temperature: this yields a hybrid transitory 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 strength⁴⁵ and precise imaging of the director throughout the bulk of the films³³ at various stages of the transition would be of great interest. Our study expands the number of available parameters one can tune to trigger transitions in shells of complex liquid crystal phases.²²

Acknowledgement The authors acknowledge Christophe Blanc and Reviewer 1 for valuable feedback that helped us narrow down the nature of the mechanism at play in this phenomenon; Lisa Tran and the rest of Randall Kamien’s group for experimental support and fruitful discussions; Kunyun He, Ashley Guo and Martina Clairand for experimental support; Bohdan Senyuk and Ivan Smalyukh for providing BTBP; Ye Zhou for useful discussions. This work was supported by the Agence Nationale de la Recherche (ANR) Grant No. 13-JS08-0006-01.

Supporting Information Available

The following data is available free of charge.

- Temperature ramp on a homeotropic 5CB cell with solid boundaries.
- Temperature-driven anchoring transition of a 5CB film in a 0.1% PVA solution in water (Supplementary Movie 1).
- Temperature ramp on a homeotropic 5CB cell with solid boundaries (Supplementary Movie 2).

- Phase transition of a 5CB film in a solution with less than 0.1 % PVA in water (Supplementary Movie 3).
- Phase transition of a 5CB shell without PVA in the inner and outer water phases (Supplementary Movie 4).
- Temperature-driven anchoring transition of typical 5CB shells, with 1 % PVA in the outer and inner phases (Supplementary Movie 5).
- 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 (Supplementary Movie 6).
- 5CB films doped with BTBP in a 0.1 % wt PVA solution undergoing a slow temperature ramp (Supplementary Figure 1).
- Additional clues pertaining to the isotropic islands (Supplementary Figure 2).

References

- (1) Jérôme, B. Surface effects and anchoring in liquid crystals. *Reports on Progress in Physics* **1991**, *54*, 391–451.
- (2) Cognard, J. *Alignment of nematic liquid crystals and their mixtures*; Gordon and Breach Science Publishers, 1982; p 77.
- (3) Miller, D. S.; Carlton, R. J.; Mushenheim, P. C.; Abbott, N. L. Introduction to optical methods for characterizing liquid crystals at interfaces. *Langmuir* **2013**, *29*, 3154–3169.
- (4) Lockwood, N. A.; Gupta, J. K.; Abbott, N. L. Self-assembly of amphiphiles, polymers and proteins at interfaces between thermotropic liquid crystals and aqueous phases. *Surface Science Reports* **2008**, *63*, 255–293.
- (5) Wang, D.; Park, S.-Y.; Kang, I.-K. Liquid crystals: emerging materials for use in real-time detection applications. *J. Mater. Chem. C* **2015**, *3*, 9038–9047.
- (6) Brake, J. M.; Daschner, M. K.; Luk, Y.-Y.; Abbott, N. L. Biomolecular Interactions at Phospholipid-Decorated Surfaces of Liquid Crystal. *Science* **2010**, *302*, 2094–2097.
- (7) Sadati, M.; Apik, A. I.; Armas-Perez, J. C.; Martinez-Gonzalez, J.; Hernandez-Ortiz, J. P.; Abbott, N. L.; De Pablo, J. J. Liquid Crystal Enabled Early Stage Detection of Beta Amyloid Formation on Lipid Monolayers. *Advanced Functional Materials* **2015**, *25*, 6050–6060.
- (8) Zhong, S.; Jang, C. H. Nematic liquid crystals confined in microcapillaries for imaging phenomena at liquid-liquid interfaces. *Soft Matter* **2015**, *11*, 6999–7004.
- (9) Khan, M.; Park, S. Y. Liquid crystal-based biosensor with backscattering interferometry: A quantitative approach. *Biosensors and Bioelectronics* **2017**, *87*, 976–983.
- (10) Gupta, J. K.; Zimmerman, J. S.; De Pablo, J. J.; Caruso, F.; Abbott, N. L. Characterization of adsorbate-induced ordering transitions of liquid crystals within monodisperse droplets. *Langmuir* **2009**, *25*, 9016–9024.
- (11) Lin, I. H.; Miller, D. S.; Bertics, P. J.; Murphy, C. J.; De Pablo, J. J.; Abbott, N. L. Endotoxin-induced structural transformations in liquid crystalline droplets. *Science* **2011**, *332*, 1297–1300.
- (12) Verma, I.; Sidiq, S.; Pal, S. K. Poly(L-lysine)-Coated Liquid Crystal Droplets for Sensitive Detection of DNA and Their Applications in Controlled Release of Drug Molecules. *ACS Omega* **2017**, *2*, 7936–7945.

- (13) Kwon, J.-Y.; Khan, M.; Park, S.-Y. pH-Responsive liquid crystal double emulsion droplets prepared using microfluidics. *RSC Advances* **2016**, *6*, 55976–55983.
- (14) Lavrentovich, O. D. Topological defects in dispersed words and worlds around liquid crystals, or liquid crystal drops. *Liquid Crystals* **1998**, *24*, 117–126.
- (15) Lopez-Leon, T.; Fernandez-Nieves, A. Drops and shells of liquid crystal. *Colloid and Polymer Science* **2011**, *289*, 345–359.
- (16) Fernández-Nieves, A.; Vitelli, V.; Utada, A. S.; Link, D. R.; Márquez, M.; Nelson, D. R.; Weitz, D. A. Novel defect structures in nematic liquid crystal shells. *Physical Review Letters* **2007**, *99*, 157801.
- (17) Lopez-Leon, T.; Koning, V.; Devaiah, K. B.; Vitelli, V.; Fernandez-Nieves, A. Frustrated nematic order in spherical geometries. *Nature Physics* **2011**, *7*, 391–394.
- (18) Urbanski, M.; Reyes, C. G.; Noh, J.; Sharma, A.; Geng, Y.; Subba Rao Jampani, V.; Lagerwall, J. P. F. Liquid crystals in micron-scale droplets, shells and fibers. *Journal of Physics: Condensed Matter* **2017**, *29*, 133003.
- (19) Lopez-Leon, T.; Fernandez-Nieves, A. Topological transformations in bipolar shells of nematic liquid crystals. *Physical Review E* **2009**, *79*, 021707.
- (20) Lopez-Leon, T.; Bates, M. A.; Fernandez-Nieves, A. Defect coalescence in spherical nematic shells. *Physical Review E* **2012**, *86*, 030702.
- (21) Noh, J. H.; Reguengo De Sousa, K.; Lagerwall, J. P. Influence of interface stabilisers and surrounding aqueous phases on nematic liquid crystal shells. *Soft Matter* **2015**, *12*, 367–372.
- (22) Tran, L.; Lavrentovich, M. O.; Durey, G.; Darmon, A.; Haase, M. F.; Li, N.; Lee, D.; Stebe, K. J.; Kamien, R. D.; Lopez-Leon, T. Change in stripes for cholesteric shells via anchoring in moderation. *Physical Review X* **2017**, *7*, 41029.
- (23) Noh, J.; Jampani, V. S. R.; Haba, O.; Yonetake, K.; Takezoe, H.; Lagerwall, J. P. Sub-second dynamic phototuning of alignment in azodendrimer-doped nematic liquid crystal shells. *Journal of Molecular Liquids* **2018**, *267*, 197–204.
- (24) Sharma, A.; Jampani, V. S. R.; Lagerwall, J. P. F. Realignment of Liquid Crystal Shells Driven by Temperature-Dependent Surfactant Solubility. *Langmuir* **2019**, *35*, 11132–11140.
- (25) Brake, J. M.; Abbott, N. L. An experimental system for imaging the reversible adsorption of amphiphiles at aqueous-liquid crystal interfaces. *Langmuir* **2002**, *18*, 6101–6109.
- (26) Poulin, P.; Stark, H.; Lubensky, T. C.; Weitz, D. A. Novel colloidal interactions in anisotropic fluids. *Science* **1997**, *275*, 1770–1773.
- (27) Poulin, P.; Weitz, D. A. Inverted and multiple nematic emulsions. *Physical Review E* **1998**, *57*, 626–637.
- (28) Sharma, A.; Lagerwall, J. P. F. Influence of head group and chain length of surfactants used for stabilising liquid crystal shells. *Liquid Crystals* **2018**, 1–10.
- (29) Noh, J.; Wang, Y.; Liang, H.-l.; Subba, V.; Jampani, R.; Majumdar, A.; Lagerwall, J. P. F. Dynamic tuning of the director field in liquid crystal shells using block copolymers. *arXiv* **2020**, 8–11.
- (30) Popov, P.; Mann, E. K.; Jáklí, A. Accurate optical detection of amphiphiles at liquid-crystal-water interfaces. *Physical Review Applied* **2014**, *1*, 034003.
- (31) Utada, A. S.; Lorenceau, E.; Link, D. R.; Kaplan, P. D.; Stone, H. A.; Weitz, D. A. Monodisperse double emulsions generated

- from a microcapillary device. *Science* **2005**, *308*, 537–541.
- (32) Sørensen, B. E. A revised Michel-Lévy interference colour chart based on first-principles calculations. *European Journal of Mineralogy* **2013**, *25*, 5–10.
- (33) Smalyukh, I. I.; Senyuk, B. I.; Gu, M.; Lavrentovich, O. D. Focused laser beams and liquid crystals: fast three-dimensional imaging of structures and topological defects. *Proceedings of SPIE* **2005**, *5947*, 594707.
- (34) Faetti, S.; Palleschi, V. Nematic-isotropic interface of some members of the homologous series of 4-cyano-4-(n-alkyl)biphenyl liquid crystals. *Physical Review A* **1984**, *30*, 3241–3251.
- (35) Faetti, S. Anchoring at the Interface Between a Nematic Liquid Crystal and an Isotropic Substrate. *Molecular Crystals and Liquid Crystals* **1990**, *179*, 217–231.
- (36) Kim, S. D.; Guo, J. K.; Song, J. K. Suspended, one-side anchored, or double-side anchored nematic droplets in an isotropic medium. *Liquid Crystals* **2016**, *43*, 1237–1243.
- (37) Kim, Y. K.; Raghupathi, K. R.; Pendery, J. S.; Khomein, P.; Sridhar, U.; De Pablo, J. J.; Thayumanavan, S.; Abbott, N. L. Oligomers as Triggers for Responsive Liquid Crystals. *Langmuir* **2018**, *34*, 10092–10101.
- (38) Ramezani-Dakhel, H.; Rahimi, M.; Pendery, J.; Kim, Y. K.; Thayumanavan, S.; Roux, B.; Abbott, N. L.; De Pablo, J. J. Amphiphile-Induced Phase Transition of Liquid Crystals at Aqueous Interfaces. *ACS Applied Materials and Interfaces* **2018**, *10*, 37618–37624.
- (39) Poincaré, H. Sur les courbes définies par les équations différentielles. *Journal de mathématiques pures et appliquées* **1885**, *1*, 167–244.
- (40) Hopf, H. Vektorfelder in n-dimensionalen Mannigfaltigkeiten. *Mathematische Annalen* **1927**, *96*, 225–249.
- (41) Seyednejad, S. R.; Mozaffari, M. R.; Ejtehadi, M. R. Confined nematic liquid crystal between two spherical boundaries with planar anchoring. *Physical Review E* **2013**, *88*, 1–6.
- (42) Koning, V.; Lopez-Leon, T.; Darmon, A.; Fernandez-Nieves, A.; Vitelli, V. Spherical nematic shells with a threefold valence. *Physical Review E* **2016**, *94*, 012703.
- (43) Zhou, Y.; Guo, A.; Zhang, R.; Armas-Pérez, J. C.; Martínez-González, J. A.; Rahimi, M.; Sadati, M.; de Pablo, J. J. Mesoscale Structure of Chiral Nematic Shells. *Soft Matter* **2016**,
- (44) Nelson, D. R. Toward a Tetravalent Chemistry of Colloids. *Nano Letters* **2002**, *2*, 1125–1129.
- (45) Yesil, F.; Suwa, M.; Tsukahara, S. Anchoring Energy Measurements at the Aqueous Phase/Liquid Crystal Interface with Cationic Surfactants Using Magnetic Fréedericksz Transition. *Langmuir* **2018**, *34*, 81–87.

Graphical TOC Entry

