Electronic Supplementary Material (ESI) for Soft Matter.
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Supporting information for "Influence of interface stabilisers and surrounding aqueous phases on nematic liquid crystal shells"

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1 Hybrid shell clearing transition observed from the side

We studied the two-step N-I transition of hybrid-aligned shells, produced with the 5CB encapsulated between WG solutions containing 1 wt.-% SDS on the outside and 1 wt.-% PVA on the inside, also from the shell side, cf. Fig. 1. This was achieved by fixing camera, hot stage and sample rigidly on the microscope, which was then tilted by 90° before the experiment was started. The camera was thus filming the shells in a direction perpendicular to the action of gravity (Fig. 1b in main paper), such that we could visualize the asymmetric shell geometry and its consequences.

Because 5CB is lighter than the aqueous phase, surrounding the liquid crystal inside and outside the shell, the shells float up to one edge of the capillary (directed upwards in the gravitational field after tilting the microscope), and within each shell the internal droplet sinks towards the bottom, making the shell thinner at the bottom than at the top. The shells are present at large enough number that one shell in the field of view of the camera could not access the capillary wall directly, but it instead rested against the first row of shells. In (a) the first transition has just initiated at the bottom of the second shell from the right, whereas all other shells pictured are still fully nematic. The first transition gradually takes place throughout the different shells in panes (b)-(d), always from bottom to top, until a fully homeotropic state is reached in all shells in (e). At a temperature about 0.05 K higher, the second transition initiates at the bottom of two shells in pane (f), gradually moving upwards and taking place also in the other shells in panes (g)-(h). In the final pane the two shells where the final transition was first detected are almost fully isotropic.

Because the shells are in contact with the glass wall of the capillary, one might think that the reason that the transition always starts at the bottom is that the glass acts as a heat sink. However, the same sequence, with each stage of the phase transition initiating at the bottom and ending at the top, is seen also in the shell that rests on other shells rather than on the capillary glass, hence any effect from the glass wall should be negligible.

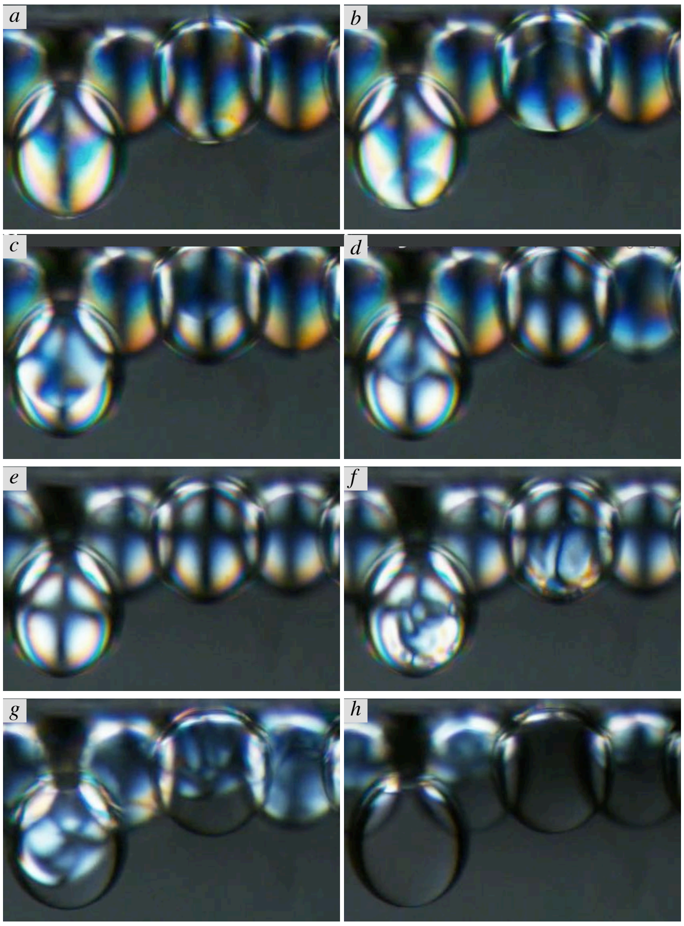

Figure 1: Sequence of images obtained in a polarising microscopy investigation (polarisers are directed vertical and horisontal) of the N-I transition in a large number of hybrid-aligned shells, viewed from the side (gravity is directed downwards). The images are frames from movie ESI 2. See text for further explanation.

It is also unlikely that the reason for the nucleation of the phase transition at the shell bottom is the defect in the director field located at the bottom of the hybrid-aligned shell. First, the shell is defect-free in the intermediate stage, where it is in a homeotropic state, and also the second stage of the phase transition nucleates from the bottom. Second, the top of the shell contains a defect in the initial hybrid-aligned state, hence we would expect nucleation from the top and bottom if the defects were the transition nuclei. A more likely explanation is that the heat flow into the shell required to drive the transition is lower at the bottom than at the top, due to the smaller volume of liquid crystal that is affected.

2 Clearing transition in inverted hybrid shell

Comparing hybrid shells with inverted geometries, i.e. homeotropic outside and planar inside (as in the main paper) versus planar outside and homeotropic inside (shown in Fig. 2), the main difference is to be found in the texture at low temperatures, when the shell is entirely nematic, cf. Fig. 2a-b here in the ESI, compared to Fig. 1a-b in the main paper. While the hybrid nematic texture shown in the main paper exhibits a characteristic texture with pink and green concentric rings around the central +1 defect, the corresponding texture in Fig. 2a-b is more uniform in color, in this respect reminding of the texture of a regular planar-aligned shell.

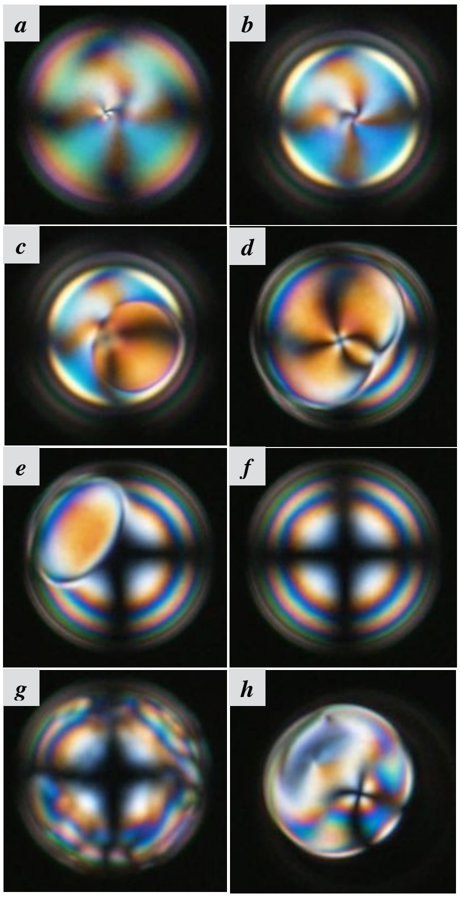

Figure 2: Sequence of textures of hybrid-aligned 5CB shell with homeotropic inside and planar outside, as it is heated through the clearing transition (from $a \rightarrow h$).

We can understand the difference in texture by considering the director field along a vertical cross section, as drawn schematically for both hybrid geometries in Fig.3. Due to the asymmetry in the shell geometry, resulting from the slightly more dense inner phase which brings the internal droplet closer to the bottom than to the top, and assuming

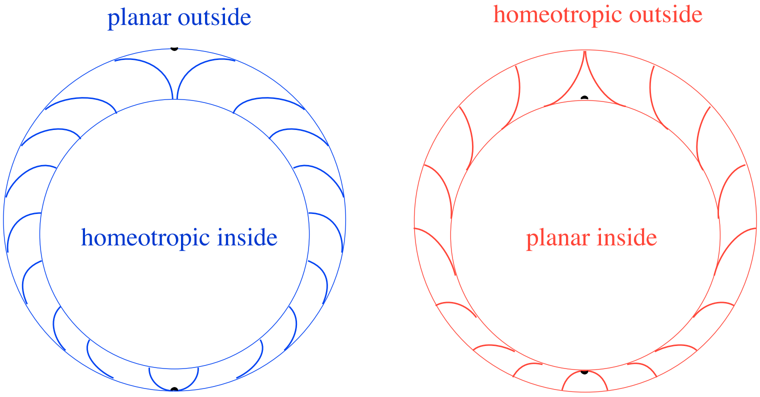

Figure 3: Schematic drawings of director field in a hybrid shell with planar outside and homeotropic inside (left), and with homeotropic outside and planar inside (right), respectively.

the same combination of radial and hyperbolic hedgehog defects, at the thinnest and thickest points of the shells, respectively, as considered by Lopez-Leon and Fernandez-Nieves, [1] we see that the thicker part of the shell is predominantly planar-aligned in case of a planar-aligning outer phase (with PVA as shell stabilizer), whereas homeotropic director orientation dominates when SDS is in the outer phase, inducing homeotropic outer boundary.

Since the thicker part of the shell gives the major contribution to the observed birefringence, regardless of what part of the shell is in focus, we can thus understand why the combination of planar outside and homeotropic inside boundaries yields a texture reminiscent of fully planar-aligned shells. Likewise, the rings seen for the opposite hybrid geometry, discussed in the main paper, result from the dominance of hometropic alignment, which in shell geometry leads to an effective birefringence that increases rapidly with distance from the center (as seen from above), producing the rings seen both in fully homeotropic shells and in the hybrid shell with planar inside and homeotropic outside.

As the shell in Fig. 2 goes through the transition to isotropic phase, the process is qualitatively identical to that described in the main paper, for hybrid shells of the opposite geometry. First the planar-aligned side (here the outside) turns isotropic at the bottom, leading to a reduction of birefringence but still a planar-like texture (Fig. 2c-d), and the clearing of the shell outside then completes at the top, changing the appearance to a classic homeotropic cross and rings texture (Fig. 2f). At slightly higher temperature, also the homeotropic side starts clearing, leading to a 'melting' of the cross texture (Fig. 2g), and at the final stage of the transition a planar-aligned drop of nematic with a visible +1 defect is seen, before the shell turns entirely isotropic.

3 Expected alignment between the two clearing points in shells with asymmetric boundary conditions

In the temperature range between the two clearing points, the remaining nematic phase is confined between the adsorbed surfactant layer and the inner volume of 5CB that has turned isotropic. The energy of the latter interface is minimised for an angle of about 60° away from homeotropic alignment,[2] and one might thus expect a hybrid alignment also here. However, the anchoring energy between isotropic and nematic phases of the same material is low, most likely much lower than the elastic energy cost of a bent director field in the thin remaining nematic phase. This would explain why no hybrid alignment is seen at this stage.

4 Shells stabilized by SDS at very low concentration

At very low SDS concentration, the surfactant cannot ensure homeotropic alignment of the liquid crystal shell. Therefore, even with SDS in both surrounding WG solutions, we found hybrid alignment when $c_{SDS} = 0.0625$ wt.-% (2.2 mM), cf. Fig. 4a. We conjecture that this SDS concentration is in the threshold regime, above which the interface coverage by SDS is sufficient to drive homeotropic alignment, while concentrations below the threshold yield a too sparse coverage to overcome the planar-aligning influence of the glycerol-water mixture.

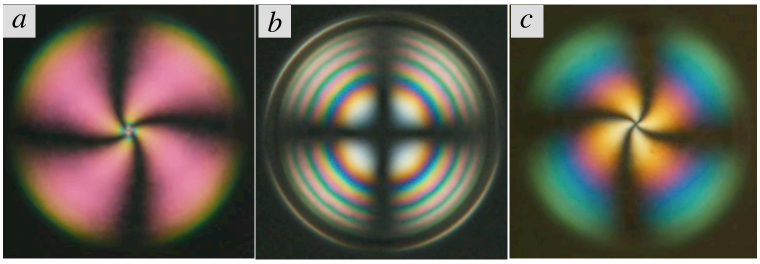

Figure 4: 5CB shells surrounded by solutions of SDS in WG, at varying concentrations. In (a), $c_{SDS} = 0.0625$ wt.-% on both sides, in (b) $c_{SDS} = 0.125$ wt.-% on both sides, while in (c) $c_{SDS} = 0.0625$ wt.-% on the outside but $c_{SDS} = 0.125$ wt.-% inside. Photo (b) shows that $c_{SDS} = 4.4$ mM is sufficient to drive homeotropic alignment throughout the shell, hence the inside of the shell must be homeotropic also in (c). However, in that photo, as well as in (a), the texture reveals hybrid alignment, hence the outside apparently becomes planar at $c_{SDS} = 0.0625$ wt.-%

The hybrid alignment in (a) indicates that the slight increase in surface area from the inside to the outside is enough to go from above to below the threshold, yielding planar-aligned outside while the inner interface is homeotropic-aligned. To confirm this, we also studied a shell with $c_{SDS} = 0.125$ wt.-% in the inside phase in two configurations. First, when also the outer phase has $c_{SDS} = 0.125$ wt.-% we get a fully homeotropic shell (Fig. 4b), hence this SDS concentration is above the threshold for ensuring that homeotropic anchoring minimizes the free energy. When such a shell was transferred to an outer solution with $c_{SDS} = 0.0625$ wt.-%, the texture changed to hybrid, as seen in Fig. 4c. The inside is clearly still homeotropic but due to the reduced SDS concentration on the outside the alignment switches to planar there.

5 Conjectured explanation for the final textural transition in hybrid shells

A detailed investigation of the origin of the textural transformations during the final step of the clearing transition in hybrid shells is beyond the scope of this paper, but we can propose a plausible scenario. Fig. 5 shows representative textures together with schematic drawings of the conjectured cross section, as seen from the side. Fig. 5a represents the surfactant-stabilised nematic phase with homeotropic alignment on the shell outside after the first transition.

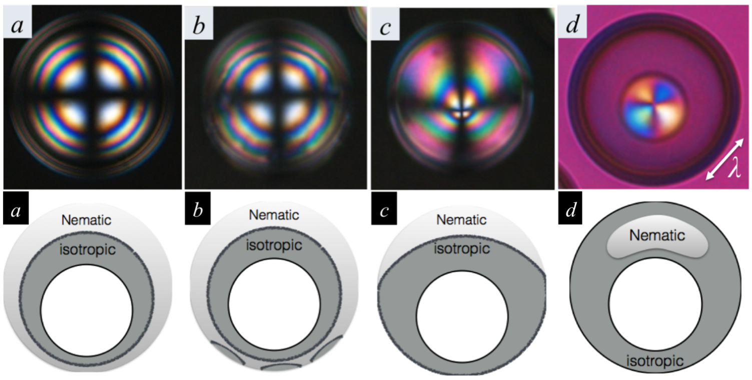

Figure 5: A sequence of polarising microscopy top view images with drawings of suggested cross-sectional side view during the second transition in hybrid shells. (a) Surfactant-stabilised nematic phase with homeotropic alignment on the outer shell. (b) Homeotropic layer breaks down as second transition is initiated at the bottom. (c) Nematic is partially detached from surfactant layer and collects into a single continuous phase, with planar-aligned bottom in contact with isotropic 5CB. (d) The remaining nematic shrinks into a smaller droplet fully detached from the surfactant-covered interface.

Because the shell is thinnest at the bottom, the stabilised nematic starts to break down from the bottom when the shell is heated, cf. Fig. 5b, the second transition nucleating at several points. To minimise interfacial energy, the newly nucleated isotropic phase regimes on the outside merge with the isotropic phase on the shell inside, Fig. 5c.

Moreover, the finally remaining nematic phase detaches from the shell outside in order to adopt a spherical interface with the isotropic phase, minimising the interfacial energy, cf. Fig. 5d. Such a detachment would explain the appearance of the +1 defect, as a result of the remaining nematic phase now being confined in a droplet completely surrounded by isotropic 5CB, inducing predominantly planar alignment.[2] The stabilised nematic may tend to expel dissolved water, glycerol and/or surfactant to the isotropic part of the shell, explaining why it exhibits the highest clearing point.

6 Movie descriptions

- **Movie ESI 1**. Heating from fully nematic to fully isotropic of a hybrid-aligned 5CB shell, with 1 wt.-% SDS in WG solution outside and 1 wt.-% PVA in WG solution inside. The texture photos in Fig. 1 of the main paper are extracted from this movie. Since the heating rate was very low, the movie has been sped up 2 times, and the sequence in which the shell stayed in homeotropic alignment, without textural changes, has been cut out.
- **Movie ESI 2**. Heating from fully nematic to fully isotropic of a hybrid-aligned 5CB shell, with 1 wt.-% SDS in WG solution outside and 1 wt.-% PVA in WG solution inside, viewed from the side. The texture photos in Fig. 1 are extracted from this movie. Since the heating rate was very low, the movie has been sped up (varying amounts in different points, up to 8 times, adjusted to an optimal viewing of the events).
- **Movie ESI 3**. Heating from fully nematic to fully isotropic of a homeotropic-aligned 5CB shell, with 1 wt.-% SDS in WG solution outside and inside. The texture photos in Fig. 2 of the main paper are extracted from this movie. Since the heating rate was very low, the movie has been sped up 2 times.
- **Movie ESI 4**. Heating from fully nematic to fully isotropic of a planar-aligned 5CB shell, with 1 wt.-% PVA in WG solution outside and inside. The texture photos in Fig. 3 of the main paper are extracted from this movie. Since the heating rate was very low, the movie has been sped up 2 times.

References

[1] T. Lopez-Leon and A. Fernandez-Nieves, “Topological transformations in bipolar shells of nematic liquid crystals,” *PHYSICAL REVIEW E*, vol. 79, no. 2, p. 021707, 2009.

[2] S. Faetti and V. Palleschi, “Nematic-isotropic interface of some members of the homologous series of 4-cyano-4-(n-alkyl) biphenyl liquid crystals,” *Physical Review A*, vol. 30, no. 6, p. 3241, 1984.