

## Electronic Supplementary Information for *Structure of the cholesteric-isotropic interface*

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### 1 Model and Methods

The starting point of our analysis is the Landau-de Gennes free energy for a cholesteric liquid crystal (LC)<sup>1,2</sup>, which is built from the usual expansion in the lowest order terms of the symmetric, traceless, tensor order parameter  $Q_{ij}$ , split into elastic  $f_e$ , and bulk terms  $f_b$ ,  $F = \int dV (f_e + f_b)$ . Here  $f_e = \frac{1}{3+2\kappa}(Q_{ij,k}Q_{ji,k} + 4q_0Q_{il}\epsilon_{ijk}Q_{kl,j} + 4q_0^2Q_{ij}Q_{ji} + \kappa Q_{ij,j}Q_{ki,k})$  and  $f_b = \frac{2}{3}\tau Q_{ij}Q_{ji} - \frac{8}{3}Q_{ij}Q_{jk}Q_{ki} + \frac{4}{9}(Q_{ij}Q_{ji})^2$ , where summation over repeated indices is assumed. Our version uses dimensionless quantities and thus the free-energy depends on only three parameters,  $\tau$ ,  $q_0$ , and  $\kappa$ .  $\tau$  is a reduced temperature whose value determines the equilibrium bulk phase. While for a nematic  $\tau = 1$  is the coexistence temperature between the nematic and the isotropic phases, for a cholesteric the coexistence temperature depends both on  $\kappa$  and the pitch (see section 2).  $q_0 \equiv \frac{2\pi}{P}$  is the inverse of the pitch  $P$ . In this model the nematic phase is described by the limit of infinite pitch  $P \rightarrow \infty$  or, equivalently, the limit  $q_0 \rightarrow 0$ . All lengths are measured in units of the correlation length  $\xi$ , which is the scale of the typical size of the topological defects and of the width of the LC-isotropic interface (typically a few correlation lengths). As a reference, for the nematic LC 5CB the correlation length at room temperature is around  $15nm$  so  $P = 1000\xi$  is equivalent to  $P = 15\mu m$ . The order in the LC phase is described by a scalar order parameter  $S$  with values  $S = 0$  in the isotropic phase and  $S = S_b$  in the LC phase. For a nematic, at the coexistence temperature,  $S_b = 1$ . For cholesterics, however,  $S_b$  depends weakly on  $\kappa$  and  $P$ .  $\kappa \equiv \frac{L_2}{L_1}$ , where  $L_1$  and  $L_2$  are the usual elastic constants of the Landau-de Gennes theory. These do not show up explicitly in our free-energy because we use a dimensionless version. The usual elastic constants of the Frank-Oseen theory  $k_1$  (splay),  $k_2$  (twist), and  $k_3$  (bend) are related to  $S_b$ ,  $L_1$ , and  $L_2$  by  $k_1 = k_3 = 9S_b^2 \frac{2L_1 + L_2}{4}$  and  $k_2 = 9S_b^2 \frac{L_1}{2}$ . Notice that this simplest version of the Landau-de Gennes theory only has two elastic constants and  $k_1 = k_3$ . Also notice that  $\kappa = 0$  is equivalent to  $L_2 = 0$  and  $k_1 = k_2 = k_3$ , known as the one-elastic-constant approximation.

We assume translational invariance along the  $z$  direction and thus calculate the configuration on the  $xy$  plane. The Landau-de Gennes free energy is minimized using the Finite Element Method with a relaxation scheme, through the commercial program COMSOL 3.5a (<http://www.comsol.com>). The meshes used are such that the precision of our numerical results is better than 1%. To

ensure a good resolution of the interface we use a finer mesh of maximum size  $\xi$  close to it.

To obtain the configurations shown in Fig. 1 of the paper we started with an initial configuration of a bulk cholesteric that changes abruptly to an isotropic phase perpendicular to the “layers”. The system is then allowed to evolve towards the minimum of the free energy.

## 2 Results for the coexistence temperature, the scalar order parameter, and the surface tension

To study interfacial phenomena we must be at the coexistence between the two phases. This is defined as the temperature at which the two phases have the same free-energy. Mathematically this is calculated by minimizing the free energy. The local minima correspond to the stable or metastable phases and we can identify the minima corresponding to the isotropic and the cholesteric phases and calculate the temperature at which these phases have the same free energy. Following the same method as Wright and Mermin<sup>3</sup>:

$$\tau_c = 1 - 3q_k^2 - \frac{1 - (1 + 2q_k^2)^{3/2}}{2}. \quad (1)$$

where  $q_k \equiv \frac{q}{\sqrt{3+2k}}$ .

The equilibrium value of the scalar order parameter in the cholesteric phase is  $S = A/4 + 3B/4$ , where  $A$  and  $B$  are

$$A = 1 - \frac{q_k^2}{2} - \frac{1 - \sqrt{9 - 8\tau - 12q_k^2 + 4q_k^4}}{4}, \quad (2)$$

$$B^2 = \frac{9}{8} - \frac{\tau}{2} + \left(\frac{3}{8} + \frac{q_k^2}{12}\right) \sqrt{9 - 8\tau - 12q_k^2 + 4q_k^4} - \frac{q_k^2}{2} - \frac{q_k^4}{6}. \quad (3)$$

To estimate the surface tension of a nematic-isotropic interface we use an ansatz,<sup>4,5</sup> where the LC has a fixed orientation relative to the interface (for example, planar or perpendicular) and we allow a change in the scalar order parameter  $S$  of the form:

$$S(y) = \frac{1}{2} \left[ \tanh\left(\frac{y}{y_0}\right) + 1 \right] \quad (4)$$

which describes an interface parallel to the  $x$ -axis, at  $y = 0$ , and with width  $y_0$ . Using this ansatz in the Landau-de Gennes free energy and minimizing with respect to  $y_0$  we obtain the scalar order parameter profile at the interface, an example of which is represented in Fig. 1. By definition, the free-energy of this profile is the surface tension. The result for the surface tension with planar anchoring is

$$\sigma_{\parallel} = \frac{1}{6} \sqrt{\frac{6 + \kappa}{3 + 2\kappa}} \quad (5)$$

and for homeotropic (perpendicular) anchoring is

$$\sigma_{\parallel} = \frac{1}{6} \sqrt{2}. \quad (6)$$

These are the results plotted in Fig. 2 of the paper (black lines). Numerically we obtain the same values, within the accuracy of the method. If we do the same calculation with other angles for the anchoring we conclude that the parallel and the homeotropic anchorings are always the maximum and minimum interfacial energies for a given value of  $\kappa$ . The minimum energy is obtained with parallel anchoring for  $\kappa > 0$  and with homeotropic anchoring for  $\kappa < 0$ . Thus, within this simplest Landau-de Gennes theory it is not possible to obtain other values for the anchoring, as discussed in the main paper.

For a cholesteric with the layers perpendicular to the interface the complex distortions close to the interface make the definition of what is the interface and the surface tension somewhat subtle. There can be two, apparently opposed, points of view on what is the interface and how to calculate the surface tension. Perhaps the most intuitive is: for  $P \gg \xi$  the cholesteric-isotropic interface is similar to the nematic-isotropic interface, including the value of the surface tension. We used this reasoning to justify why the surface tension of a cholesteric with planar alignment at the interface, as in Fig. 1, has the same value as the nematic-isotropic surface tension. From this point of view the undulation of the interface and the distortions of the cholesteric layers are not part of the interface and should not be included in the calculation of the surface tension.

At the macroscopic scale the interface is effectively flat. Notice that the amplitude of the undulations in Fig. 1 of the paper is a small fraction of the pitch. For pitches on the micron scale the undulations of the interface are most likely below the visible wavelengths and the interface will appear flat when observed with an optical microscope. For example in Agez *et al.*<sup>6</sup> the undulations can only be resolved with an AFM and are in a range between 20 and 100 *nm*. From a thermodynamic, macroscopic, point of view the surface tension is the free energy cost of increasing the area of an interface. This means that if we double the area of the interface, we must double the number of distortions. Hence, the energetic contributions of the undulations and of the distortions of the cholesteric layers must be included in the free energy. They are an integral part of the interface.

As we just discussed, the definition of the interface and the surface tension depends on the length scale at which we look at the system. We are interested in the thermodynamic surface tension and so we adopt the thermodynamic view. To calculate the surface tension for given pitch  $P$  and  $\kappa$  we note that the free energy is constructed such that at coexistence the free energy of the LC and that of the isotropic phase are equal and correspond to the ground-state, and thus the thermodynamic surface tension is simply the volume integral of the free energy of the configuration that minimizes the free energy, such as those shown on Fig. 1 of the paper.

As also discussed in the paper the value of  $\kappa$  at which the preferred anchoring changes from homeotropic to parallel depends on the pitch. Fig. 2 plots the phase diagram of the anchoring as a function of both the pitch and  $\kappa$ .

## References

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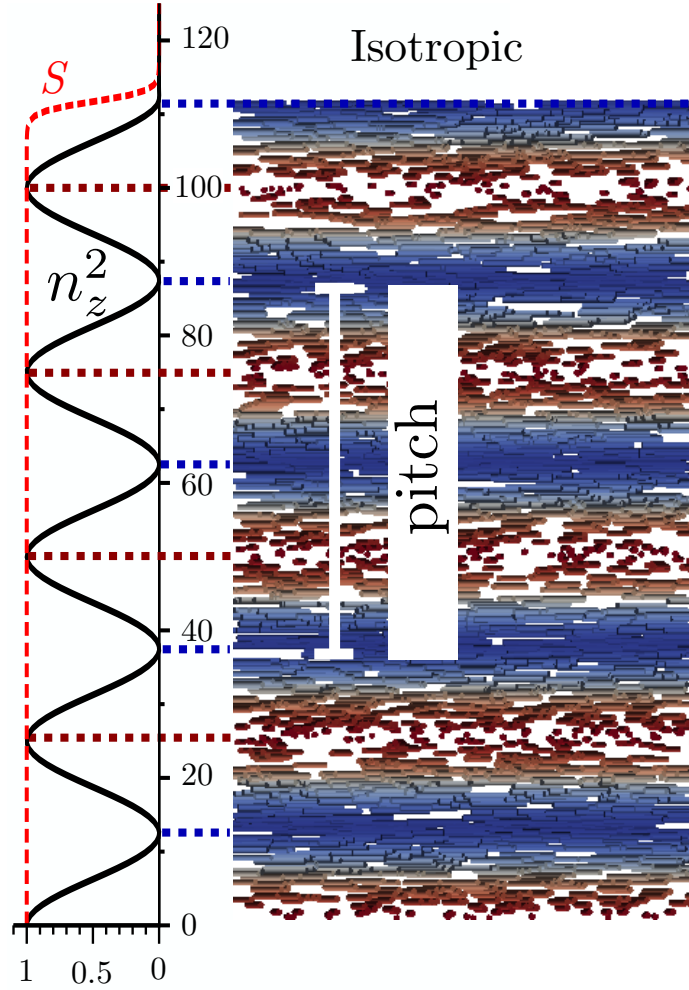


Figure 1: Cholesteric-isotropic interface with planar anchoring. The cholesteric has a pitch  $P = 50\xi$  and the local orientation of the LC is given by the orientation of the cylinders and color coded from in-plane (blue) to out-of-plane (red). Also plotted are the values of the scalar order parameter  $S$  (red dashed line) and the out-of-plane orientation of the LC  $n_z^2$  (black line) along the vertical direction. The interface is identified by the abrupt change (a few correlation lengths) in the value of  $S$  from  $S_b \approx 1$  to 0.

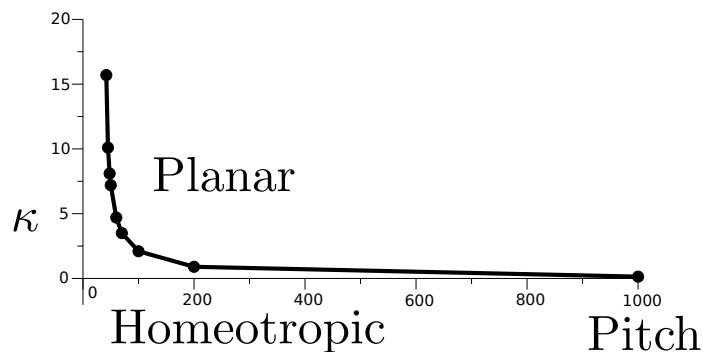


Figure 2: Anchoring of a cholesteric at an interface with the isotropic phase. For a nematic (infinite pitch) the boundary between planar and homeotropic anchoring is at  $\kappa = 0$ . For a cholesteric the boundary shifts to  $\kappa > 0$ . For  $P = 100\xi$ ,  $\kappa = 2.1$  and for  $P < 42$  we could not find a value above which planar anchoring is preferred.

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