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Surface Anchoring Energy of Cholesteric Liquid Crystals

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Abstract

In this paper, we propose a suitable surface energy expression for cholesteric liquid crystals. We show that there exists a symmetry allowed term for chiral nematics that doesn't appear in the traditional Rapini-Papoular surface energy form. We discuss some consequences of this new surface anchoring term.

Keywords: surface anchoring; cholesteric liquid crystal; symmetry

1 Introduction

In this paper, we consider the surface energy density of cholesteric liquid crystals (CLCs). Symmetry arguments have been successfully used to predict novel phenomena in liquid crystals [1]. Using symmetry arguments, we show that in addition to the standard Rapini-Papoular form [2], a new additional term exists, which may change the behavior of cholesteric samples.

Symmetry arguments rely on tensor representations which allow coordinate-system independent covariant expressions to be formed. One identifies the relevant tensor quantities and then inquires how these can be combined to form an expression with the right tensor properties. All physical quantities are tensors of different rank; scalars are rank zero, vectors are rank one, and so on. Tensors are either 'proper' or 'pseudo-'; components of proper tensors of even rank do not change sign under parity (centro-inversion of the coordinate system) but those of odd rank do, while components of pseudotensors of odd rank do not change sign under parity, but those of even rank do. Basic physical quantities (length, mass, time, temperature, electric current) are proper; other quantities derived from these may be proper, such as energy, force, electric field, and dielectric permittivity, or pseudo, such as torque, angular momentum, and magnetic field.

Symmetry arguments are based on two key points. If the quantity of interest with the right property (proper or pseudo) cannot be constructed from the set of relevant quantities, then the existence of the quantity of interest arising from the relevant quantities is forbidden by symmetry, and the corresponding process cannot occur. If the quantity of interest with the right property (proper or pseudo) can be constructed from the set of relevant quantities, then the quantity of interest is allowed by symmetry, and will consequently occur in general.¹

The paper is organized as follows. In Section 2, a new term in the surface anchoring energy of cholesteric liquid crystals is proposed using a symmetry argument. We summarize and conclude the paper in Section 3.

2 Surface anchoring energy

Liquid crystals are characterized by orientational order. Orientational order can be modeled in a variety of ways; here we begin by using the order parameter tensor formalism. The orientation of liquid crystal

¹Totalitarianism has been adopted as a principle of physics; according to Gell-Mann "Everything not forbidden is compulsory." [3]

molecules is described by a unit vector $\hat{\mathbf{l}}$, and the order parameter tensor $Q_{\alpha\beta}$ is defined by

$$Q_{\alpha\beta} = \left\langle \frac{1}{2}(3l_\alpha l_\beta - \delta_{\alpha\beta}) \right\rangle, \quad (1)$$

where $\langle \rangle$ denote ensemble average. The order parameter tensor is symmetric and traceless, it may be uniaxial with two identical eigenvalues, or biaxial, where all three eigenvalues are different.

Since liquid crystals are soft, for large samples, bulk orientation is dominated by surface interactions. Surface anchoring is therefore of paramount importance both in fundamental studies and also in device applications.

We now use symmetry arguments to construct the allowed surface anchoring energy of nematic liquid crystals. In order to identify the relevant quantities, we consider the interaction of nematic molecules with a substrate. There are both steric and attractive interaction with the substrate, as with other liquid crystal molecules in the bulk. For this reason, it has been proposed that the substrate may be regarded as consisting of ‘frozen’ liquid crystal molecules, with some given order parameter tensor $Q_{\alpha\beta}^0$ [4]. Using this, we identify the relevant quantities to form the surface anchoring energy density as the liquid crystal order parameter $Q_{\alpha\beta}$, the surface normal unit vector N_α , and the preferred anchoring order parameter at the substrate $Q_{\alpha\beta}^0$.

The order parameters can be written in different forms, choice is a matter of convenience. We note that the liquid crystal order parameter can be written as

$$Q_{\alpha\beta} = \lambda_1 n_\alpha n_\beta + \lambda_2 m_\alpha m_\beta, \quad (2)$$

or

$$\mathbf{Q} = \lambda_1 \hat{\mathbf{n}}\hat{\mathbf{n}} + \lambda_2 \hat{\mathbf{m}}\hat{\mathbf{m}}, \quad (3)$$

where $\hat{\mathbf{n}}\hat{\mathbf{n}}$ is a dyad, the tensor product of the nematic director $\hat{\mathbf{n}}$ with itself. If the system is biaxial, director defining the direction of the minor axis is $\hat{\mathbf{m}}$. Similarly, we write for the preferred anchoring order parameter at the substrate $Q_{\alpha\beta}^0$ as

$$\mathbf{Q}^0 = \lambda_1^0 \hat{\mathbf{n}}^0 \hat{\mathbf{n}}^0 + \lambda_2^0 \hat{\mathbf{m}}^0 \hat{\mathbf{m}}^0, \quad (4)$$

and we have the surface normal $\hat{\mathbf{N}}$.

2.1 Achiral nematics

Here we consider achiral nematics, where both the phase and the particles have inversion symmetry. We next consider forming the surface anchoring energy density, a proper scalar, from the relevant quantities $Q_{\alpha\beta}$, N_α and $Q_{\alpha\beta}^0$. We can construct, to lowest order in $Q_{\alpha\beta}$, three non-zero terms. We list all of these in the expression for the achiral anchoring energy density

$$\mathcal{E}_a = \frac{1}{2} W_1 Q_{\alpha\beta} Q_{\alpha\beta}^0 + \frac{1}{2} W_2 Q_{\alpha\beta} N_\alpha N_\beta + \frac{1}{2} W_3 Q_{\alpha\beta} N_\alpha Q_{\beta\gamma}^0 N_\gamma. \quad (5)$$

This can be written more simply as

$$\mathcal{E}_a = \frac{1}{2} W_1 \mathbf{Q} : \mathbf{Q}^0 + \frac{1}{2} W_2 \mathbf{Q} : \hat{\mathbf{N}}\hat{\mathbf{N}} + \frac{1}{2} W_3 (\mathbf{Q} \cdot \hat{\mathbf{N}}) \cdot (\mathbf{Q}^0 \cdot \hat{\mathbf{N}}), \quad (6)$$

and if the system is uniaxial, we recover

$$\mathcal{E}_a = \frac{1}{2} W_1' (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0)^2 + \frac{1}{2} W_2' (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})^2 + \frac{1}{2} W_3' (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}}) (\hat{\mathbf{n}}^0 \cdot \hat{\mathbf{N}}) (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0), \quad (7)$$

which has the usual Rapini-Papoular form if $\hat{\mathbf{n}}^0$ is in the plane of the substrate (that is, where $\hat{\mathbf{n}}^0 \cdot \hat{\mathbf{N}} = 0$), while the third describes anchoring energy with pre-tilt.

If the rubbing direction is in the plane of the surface, the director will align either along the surface normal $\hat{\mathbf{N}}$ or the rubbing direction $\hat{\mathbf{n}}^0$. If rubbing is not in the plane, the third term allows the director to orient in other directions.

2.2 Chiral nematics

Now we turn to the central point of our paper, surface anchoring of chiral nematic or cholesteric liquid crystals. The novel aspect of cholesterics is broken inversion symmetry due to the chirality of the constituent molecules. Since chiral objects lack inversion symmetry, it is possible to associate three non-collinear proper vectors with chiral systems. The three proper vectors \mathbf{A} , \mathbf{B} and \mathbf{C} can be combined to form the pseudoscalar $\mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})$. Since the converse is also true, (a handed vector triad can be constructed if a pseudoscalar exists), pseudoscalars are indicators of chirality. In the case of cholesteric liquid crystals, a pseudoscalar q_0 is often used to represent the intrinsic twist in the orientation of molecules, with $q_0 > 0$ for right-handed chirality, and $q_0 < 0$ for left-handed chirality. The wavelength of the periodicity of the system is the pitch $p = 2\pi/|q_0|$. With a pseudoscalar q_0 in the system, one can construct one additional proper scalar term, arising from chirality, in the surface anchoring energy density. The new term, in addition to the ones in Eq. (5), is

$$\mathcal{E}_c = \frac{1}{2} q_0 W_c \varepsilon_{\alpha\beta\gamma} Q_{\mu\beta} N_\gamma Q_{\mu\alpha}, \quad (8)$$

where $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita antisymmetric tensor. The energy \mathcal{E}_c is a proper scalar, allowed by chirality and the presence of the pseudoscalar q_0 . Explicitly, in terms of the eigenvectors, it becomes

$$\begin{aligned} \mathcal{E}_c = & \frac{1}{2} q_0 \{ W_{c1} \hat{\mathbf{n}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{n}}) (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0) + W_{c2} \hat{\mathbf{m}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{n}}) (\hat{\mathbf{n}} \cdot \hat{\mathbf{m}}^0) \\ & + W_{c3} \hat{\mathbf{n}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{m}}) (\hat{\mathbf{m}} \cdot \hat{\mathbf{n}}^0) + W_{c3} \hat{\mathbf{m}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{m}}) (\hat{\mathbf{m}} \cdot \hat{\mathbf{m}}^0) \}. \end{aligned} \quad (9)$$

We note that the energy \mathcal{E}_c , a proper scalar, does not change sign under centroinversion.

In the uniaxial case, the above expression simplifies to

$$\mathcal{E}_c = \frac{1}{2} q_0 W_{c1} \hat{\mathbf{n}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{n}}) (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0), \quad (10)$$

which clearly shows the contribution of chirality to the anchoring energy. The geometry is shown in Fig. 1 for the case when the rubbing direction $\hat{\mathbf{n}}^0$ is in the plane of the substrate.

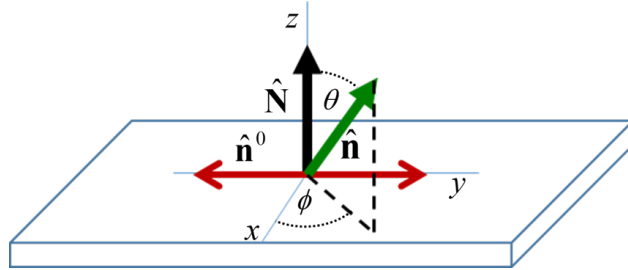


Figure 1: A schematic showing the cholesteric liquid crystals and a substrate. Here $\hat{\mathbf{N}}$ represents outward surface normal, $\hat{\mathbf{n}}^0$ is the rubbing direction, and $\hat{\mathbf{n}}$ is the chiral nematic director.

In terms of the angles, the new term due to chirality becomes

$$\mathcal{E}_c = \frac{1}{2} q_0 W_{c1} \sin^2 \theta \sin 2\phi, \quad (11)$$

which is minimized when the director is at 45° or 135° from the x -axis, the direction depends on the sign of the coefficient. When the rubbing direction $\hat{\mathbf{n}}^0$ is in the plane of the substrate, the total energy is given by

$$\mathcal{E}_t = \frac{1}{2} W_1' (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0)^2 + \frac{1}{2} W_2' (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})^2 + \frac{1}{2} q_0 W_{c1} \hat{\mathbf{n}}^0 \cdot (\hat{\mathbf{N}} \times \hat{\mathbf{n}}) (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}^0). \quad (12)$$

The minimum energy is obtained when the director is either along the normal $\hat{\mathbf{N}}$, or perpendicular to it, along $\hat{\mathbf{n}}^0$. In the latter case, the equilibrium orientation of the director will differ from the rubbing direction. The magnitude of the deviation depends on the relative strengths of the surface interactions, and direction of the deviation is the opposite for right- and left-handed systems.

Dimensional analysis suggests that the ratio of W_{c1}/W_1 is small, of the order of the molecular length l_0 to the pitch p . This is only a conjecture, however, to be verified by experiment. Many chiral nematic systems consist of achiral nematic molecules mixed with chiral dopants. It is expected that in such systems, due the presence of the new anchoring term, the concentration of chiral dopants may be different at the surface than at the bulk. Verifying this may be another experimental verification of our model.

We note that our strategy used above can be adapted to other systems. For example, in a bulk chiral liquid crystal elastomer with strain, one can construct an energy term similar to that in Eq. (8), where the strain tensor plays the role of \mathbf{Q}^0 and, say, the electric field the role of $\hat{\mathbf{N}}$. Such a term predicts a linear mechanical response of cholesteric elastomers to an applied electric field.

3 Summary

In this paper, we propose a general form of surface anchoring energy of chiral liquid crystals. Explicitly, we argue that in addition to existing terms in the literature, there exists a new symmetry allowed term in the surface anchoring energy density. Chirality leads to the deviation of the director at equilibrium from the rubbing direction. Our results may also be useful for novel applications of chirality-induced phenomena [5], and our strategy may be useful in predicting novel phenomena in chiral systems.

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