

Formation of liquid-crystal cholesteric pitch in the centimeter range

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The formation of a macroscopic cholesteric spiral in a nematic liquid crystal (LC) doped with chiral molecules is studied. Measurements of the orientation of the disclination line formed in a LC θ -cell manufactured with one substrate having linear in-plane alignment and the opposing substrate having circular alignment showed the formation of a uniform macroscopic cholesteric spiral with a pitch length of centimeters. We found a linear dependence of the reciprocal pitch p^{-1} on the concentration c in a wide range of p , extending from micrometers up to several centimeters. It suggests that the pitch of a spiral in a nematic LC doped with chiral dopants results from a long-range orientation owing to short-range chiral interactions in the vicinity of the chiral additive.

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I. INTRODUCTION

Chirality is a very general property of objects or systems, which are not superimposable on their mirror image. Chirality plays a fundamental role in physics, astronomy, chemistry, and biology (e.g., DNA molecules). It is found on every length scale, starting from the world of elementary particles to the universe where spiral galaxies are observed with opposite handedness.

On the level of molecular compositions long-distance orientational ordering in liquid crystal mesophases determines the uniqueness and diversity of their chiral properties. Chiral mesophases in liquid crystals can be formed due to the chiral structure of constituent molecules (traditional cholesteric, chiral nematic, and smectic phases) or by chiral super-structures formed by achiral molecules (e.g., chiral smectic phases and blue phases formed from bend-shaped and banana-shaped molecules) [1,2].

A well-known but still intriguing chirality effect is the formation of a chiral nematic phase upon doping of initially nonchiral nematics with small amounts of chiral molecules. The origin of this effect is closely related with the problem of transfer of chirality from chiral inclusions to an achiral nematic matrix. In his early works, de Gennes [3,4] and more recently Lev and Tomchuk [5] supposed that the inclusions distort the long-range orientation order, and the overlapping of these distortions produces a supermolecular chiral structure. This approach is valid for macroscopic chiral inclusions and for chiral molecular dopants, the size of which is comparable with the size of the LC matrix molecules. Short-scale intermolecular interactions are necessary for this effect. According to earlier reports [6,7], a short-scale chiral interaction between the chiral dopant and LC molecules induces a director twist in the vicinity of the chiral agent, which can then extend to larger distances due to long-range anisotropic correlation between LC molecules. The question is: how big can this distance be? To our knowledge, there is no definite answer to this fundamental question. In Ref [6], Berardi *et al.* studied a system in which a nematic is put in contact with a surface covered with chiral molecules that cannot diffuse into the nematic bulk, and the other contact surface is covered with achiral molecules. Nematic molecules were considered as hard rod elongated

particles, whose interaction can be described by a Gay-Berne potential with the addition of a short-range chiral contribution for the particles at the chiral surface. Monte Carlo computer simulation of this system showed that the chiral surface induces an average twist of the particles near the chiral surface that relaxes smoothly to zero under the influence of the achiral counter-surface. It is important to note that this model predicts that due to long-range orientational correlations in the nematic phase a twisted local director is conserved in the absence of the achiral counter-surface. Therefore, the model implicitly predicts extension of the twist from the chiral surface at arbitrarily large distances. This prediction [6] is a consequence of one-dimensional geometry of the considered problem. As a matter of fact, the problem of a distortion in a LC around the chiral molecule is a three-dimensional problem. Evidently, in 3D space a local orientational distortion relaxes with the distance from the distortion source. Therefore, although the dependence of the chirality distortion on the distance from a chiral dopant molecule is unknown, one may expect a finite characteristic length L_{ch} of the chirality spreading. The value of this characteristic length L_{ch} is unknown. Moreover, it is unclear if the characteristic length L_{ch} affects the properties of the macroscopic pitch p , of the director spiral in a chiral nematic. One may expect, for instance, some peculiarities in the dependence of the macroscopic pitch on the distance between chiral dopants d_{ch} when $d_{\text{ch}} \approx L_{\text{ch}}$.

In the present paper we have shown that up to giant values of the pitch $p \approx 3.5$ cm, which is more than 3 orders larger of the cell thickness, the pitch is proportional to d_{ch}^{-3} ; i.e., it is inversely proportional to the weight concentration of the dopant c . This fact shows that despite spatial relaxation of the chirality distortion, the chiral distortions in a nematic matrix are linearly additive.

II. METHOD DESCRIPTION OF A PITCH MEASUREMENT WITH θ CELL

Traditional methods of the measurements of the spiral pitch in nematic LCs (Bragg band measurements, Grandjean-Cano wedge [8]) do not allow precise measurements of the pitch larger than the LC cell thickness. To our knowledge, the largest pitch values (several hundred micrometers) were determined

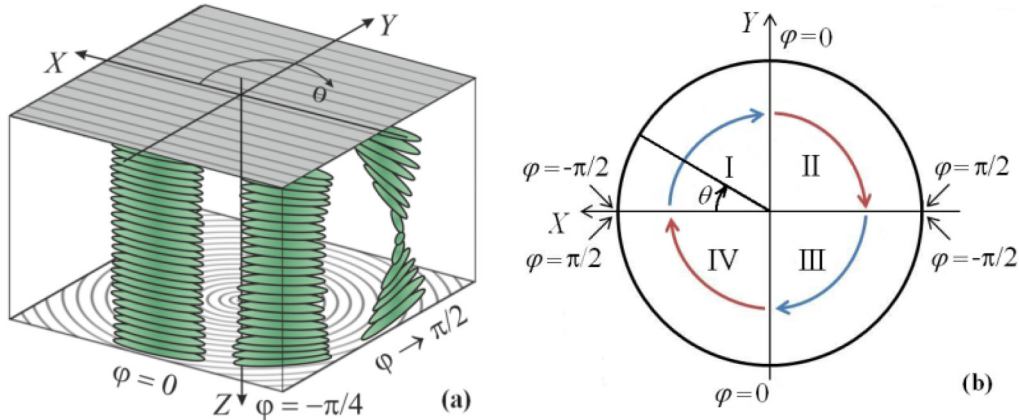


FIG. 1. (Color online) (a) Schematic view of a θ cell. Elongated ellipsoids stand for the director shown in three columns for the twist angles (0 , $-\pi/4$, and $\pi/2$). While there is no twist in the direction along the Y axis, the boundary conditions dictate $\pm\pi/2$ twist in the direction along the X axis. (b) Schematic representation of the azimuthal director distribution at the circularly aligning surface. The arrows indicate the director twist in the different quadrants of the surface: φ varies from $-\pi/2$ to 0 in the first quadrant (left twist), from 0 to $\pi/2$ in the second quadrant (right twist), from $-\pi/2$ to 0 in the third quadrant (left twist), and from 0 to $\pi/2$ in the fourth quadrant (right twist).

by the measurements of the curvature of disclination lines in a LC doped with chiral carbon nanotubes [9], but the accuracy of these measurements is not high. Our studies require measurements of as large a pitch length as possible. Therefore, we applied a method proposed initially by Suh *et al.* [10] and reinvented recently in Ref. [11]. It is based on the use of an optical element called a θ cell, proposed by Stalder and Schadt [12], and allows easy, precise, and reliable measurements of extremely large LC pitches, up to the centimeter range.

As shown in Fig. 1(a), a θ cell is constructed using one substrate with unidirectional planar alignment and the second opposing substrate with circular planar alignment. In this cell the director is twisted, and the corresponding twist angle $\varphi(z)$ depends on the azimuth angle θ .

In the case of achiral nematic LC and strong surface anchoring the minimum of the free energy corresponds to the twist angle on the circularly rubbed surface $\varphi_c = \theta - \pi/2$, which is given by the direction of rubbing at each point on the substrate [Fig. 1(a)]. The maximum value of the twist does not exceed $\pm\pi/2$. As a result, the distribution $\varphi(\theta)$ has a mirror symmetry with respect to the rubbing direction on the surface with parallel rubbing (ZX plane). The director is not deformed and it is uniformly aligned ($\varphi = 0$) only at $\theta = \pm\pi/2$ (along the ZY plane), and it is twisted in the other regions, as shown in Fig. 1(b). In the upper half-plane ($y > 0$) the director is twisted to the left in the first quadrant ($\varphi \in [-\pi/2; 0]$) and twisted to the right in the second quadrant ($\varphi \in [0; \pi/2]$). In the lower half-plane ($y < 0$), the director is twisted to the left in the third quadrant ($\varphi \in [-\pi/2; 0]$) and twisted to the right in the fourth quadrant ($\varphi \in [0; \pi/2]$). The left and right deformations collide along the x axis, where the topological conflict results in a formation of a disclination line [11–13].

Chirality of the LC changes the equilibrium configuration of the director in the cell. At $p > l$ (l is the thickness of the cell) the director is not deformed along the plane which deviates from the azimuth $\theta = \pi/2$ on the twist angle of the spiral $\delta = 2\pi l/p$ over the cell thickness. The borders between the areas with the left twist and the right twist and correspondingly

the disclination line rotate on the same angle,

$$\delta_{+,-} = \frac{2\pi l}{p_{+,-}}, \quad (1)$$

where the indices (+, -) indicate the sign of the chirality; the right spiral (+) results in a clockwise rotation of the disclination and the left spiral (-), in counterclockwise rotation.

In the case of multiple pitch within the cell ($p < l$), the disclination appears at the azimuth angle larger than 2π and

$$p_{+,-} = \frac{2\pi}{2\pi n + \delta_{+,-}} l, \quad (2)$$

where n is an integer number of the 2π rotations of the disclination line. The sign of the twist deformation is the same over the cell but the pitch experiences a half-pitch step at the disclination.

The disclination line is a stationary topological defect with a singular core. Its visible width is very thin (about $1 \mu\text{m}$) and the error in a detection of its orientation is mainly determined by the error of the positioning of the microscopic stage, not larger than $\Delta\varphi \approx 0.5^\circ$. This ensures straightforward measurement of pitches much larger than the cell thickness l . For example, for $l = 50 \mu\text{m}$, the rotation of the disclination on the minimum-detectable angle $\Delta\varphi = 0.5^\circ$ from the initial position along the X axis corresponds to the pitch $p \approx 3.5 \text{ cm}$. At the same time, the measurements of small pitches ($p < l$) is also easy since it reduces to the counting of the number of 2π -rotation of the disclination line in a set with different cell thickness. Therefore, the method allows precise measurements of the pitch in a very wide range $p = 1-10^4 \mu\text{m}$. This range and accuracy of the pitch measurement is impossible with any other known technique.

For $p > l$ the error of the pitch measurements resulting from nonuniformity of the cell thickness is negligibly small. For instance, the typical thickness irregularity $\Delta l = 0.2 \mu\text{m}$ results in rotation of the disclination line by $\delta = 0.7^\circ$ only at $p = 100 \mu\text{m}$. At the condition $p < l$ the orientation of the disclination is very sensitive to the cell thickness; for

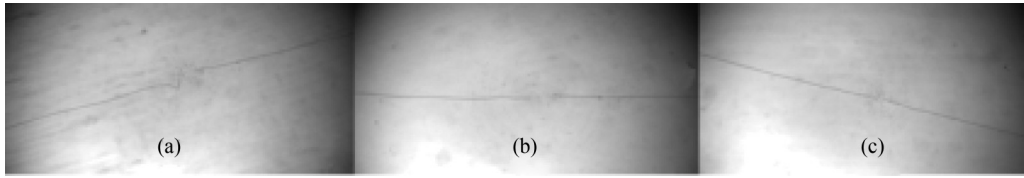


FIG. 2. Microscope view (without polarizers) of a LC cell: (a) filled with composition 5CB and R-811 (right-handed), (b) filled with pure nematic 5CB, (c) filled with composition 5CB and S-811 (left-handed). The width of the windows is about 1 mm.

$p = 1 \mu\text{m}$ the deviation of the disclination of 1° corresponds to the thickness irregularity $\Delta l \approx 3 \text{ nm}$. At the same time, this high sensitivity of the disclination orientation to the cell thickness does not result in a big error of p measurements for short pitches because in this case $p \approx l/n$ [see Eq. (2)].

III. EXPERIMENTAL

To use the method practically, we assembled an LC cell made from two glass substrates covered with the polyimide film poly-oxydiphenylene-pyromellitimide (analog of Kapton). One of the substrates was rubbed unidirectionally using a velvet cloth while the opposing substrate was rubbed circularly and clockwise. The rubbed polyimide films provided a strong planar alignment of a LC in cell. The thickness of the cell was set using 20- μm polymer spacers and monitored using the light interference pattern found in the empty cell. Then the cell was capillary filled with the LC 5CB at the temperature $T \approx 50^\circ\text{C}$ and slowly cooled down to a room temperature. During the cooling the cell was put on a metallic plate to provide a thermal contact with the circularly rubbed substrate. This ensured an extension of the nematic phase from the circularly rubbed substrate and resulted in a high-quality alignment of the LC. Several chiral dopants for different handedness were exploited to produce the twist. The used right-handed chiral dopant was *L*-menthyl biphenylcarboxylate acid (DMDA) obtained from the Institute of Single Crystals, Ukraine. The left- and right-handed chiral dopants from Merk, S811 and R811, respectively, were also studied. In all cases the pretilt angle of the LC was about 1° .

Figure 2 shows the photographs of the cell with pure LC 5CB, LC 5CB doped with the right-handed dopant (R811)

in the concentration, $c = 1.5 \cdot 10^{-4}$, and LC 5CB doped with the left-handed dopant (S811) in the same concentration. The disclination in the cell with pure 5CB is oriented exactly parallel to the rubbing direction of unidirectional aligned substrate. The disclinations in the doped LC are rotated relative to their position in the cell with pure 5CB in opposite directions on the same angle $|\delta| \approx 15^\circ$. According to Eq. (1), the angle δ corresponds to a pitch $p = 481 \mu\text{m}$. The right-handed dopant results in the clockwise rotation of the disclination and the left-handed dopant in counterclockwise rotation.

When the rotation angle $\delta \leq \pi$, the cells seen in the daylight are black and white in the crossed polarizers, owing to the Mauguin regime condition is satisfied [13]. The disclination line divides the cell into two parts, each of which, in turn, is divided in two sectors with opposite directions of twist deformations [Fig. 3(a)]. When $\delta \geq \pi$, the cells are colored due to the violation of the Mauguin regime and appearance of a dispersion for the polarization rotation. The sign of the twist is the same in every sector in this case, but the pitch makes a one-half step at the opposite sectors borders [Fig. 3(b)].

At small concentrations of the dopants that correspond to $\delta \leq 2\pi$ and the large pitches ($p \geq 20 \mu\text{m}$) the disclination lines

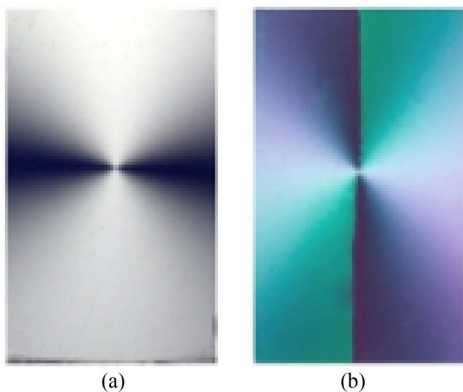


FIG. 3. (Color online) Photographs of the cells in crossed polarizers filled with a composition 5CB and S-811: (a) $c = 2.6 \times 10^{-4}$, $\varphi = 3.1 \text{ rad}$; (b) $c = 2.2 \times 10^{-3}$, $\varphi = 17 \text{ rad}$. The dimension of the pictures is $1 \times 2 \text{ cm}$.



FIG. 4. (Color online) Photograph of the cell with inhomogeneous thickness in crossed polarizers. The cells filled with composition 5CB and S-811: $c = 3.7 \times 10^{-3}$. The numbers indicate the local thickness of the cell. The dimension of the picture is $1 \times 2 \text{ cm}$. The calculated thickness of the cell along the disclination line is depicted on the figure.

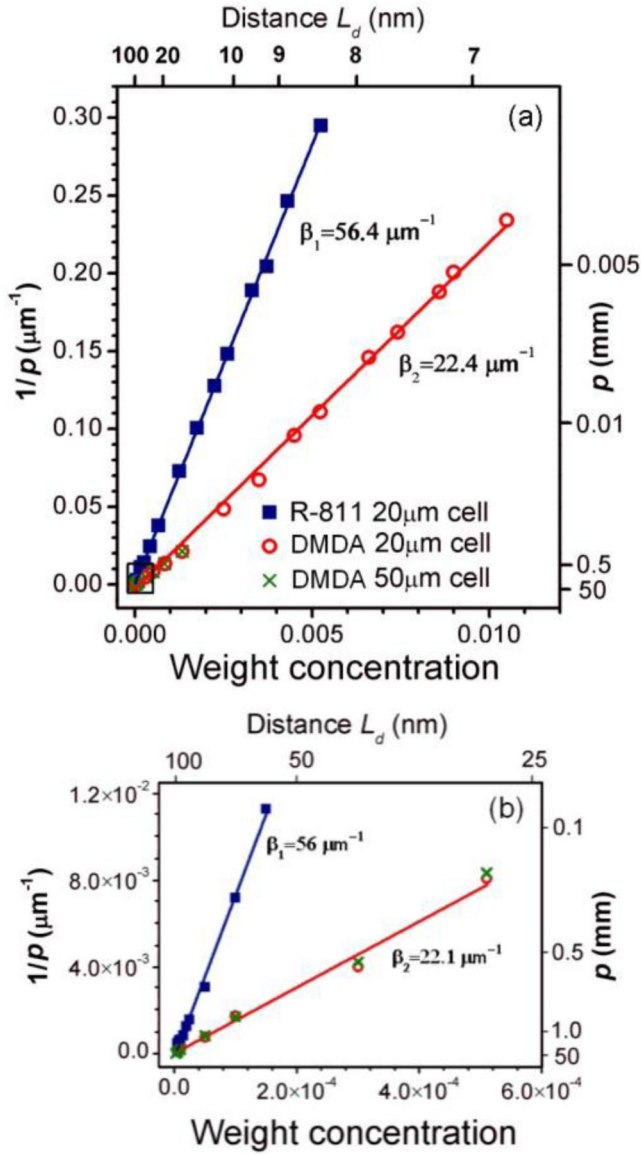


FIG. 5. (Color online) (a) The dependences of the reciprocal pitch p^{-1} on the concentration c , and an average distance between the dopant molecules L_d , for the chiral dopants DMDA and R-811. The corresponding pitch values are depicted at right. The enlarged small concentration region is depicted in (b).

are essentially straight. In the case of larger concentrations and shorter pitch, the disclinations are often curved and typically have an S -shape deformation as shown in Fig. 4. This deformation is caused by a lens-like distortion of the cell thickness. This effect was confirmed by pressing on the center of the cells with short pitch, which transformed the linear disclination into an S shape. In the case of the cell with a short pitch ($p = 4.88 \mu\text{m}$) depicted in Fig. 4, the bend of the disclination line corresponds to the difference in the cell thickness $\Delta l \approx 1 \mu\text{m}$ in the center and the periphery of the cell, and accuracy of the measurements of the cell thickness deviation at each disclination point is not less than 10 nm.

It should be noted that besides thickness irregularity, the tilt of the director on the substrates also can distort the data, as

different director configurations—parallel and antiparallel—are produced on opposite sides of the disclination lines. The difference in the elastic energy on the opposite sides of the disclination results in shift of its equilibrium position. We found that in the cell with pure 5CB and the pretilt angle on the both substrates 8° the disclination line deviated from the unidirectional rubbing on the angle $\pm(2 \pm 1)^\circ$, and the sign of the deviation depended on the direction of the unidirectional rubbing.

The dependence of the reciprocal pitch p^{-1} on the concentration c and the average distance between the dopant molecules L_d for the chiral dopants DMDA and R-811 are presented in Fig. 5. The variation in the range from $c \approx 2.5 \times 10^{-6}$ up to $c \approx 1.4 \times 10^{-3}$ correspond to a change of a pitch from $p = 3.6 \text{ cm}$ down to $4.2 \mu\text{m}$ for DMDA and from 0.8 cm down to $3.3 \mu\text{m}$ for R-811. The measurements across such a wide a range are possible only by the method described above. The experimental data were obtained using two series with cells of different thickness, which are marked in Fig. 5 by different symbols. The accuracy of the azimuth measurement at the low concentration region provides very high precision of the pitch determination ($\Delta p^{-1} \approx 10^{-4} \mu\text{m}^{-1}$) with an error less than the size of the symbols in the plot. One can see that all the data fit to the common dependence $p^{-1}(c)$. The results are described by two straight lines with different slopes corresponding to linear dependencies with slopes $\beta_1 = 56.4 \pm 0.5 \mu\text{m}^{-1}$ and $\beta_2 = 22.4 \pm 0.3 \mu\text{m}^{-1}$.

IV. DISCUSSION AND CONCLUSIONS

The concentration $c \approx 2.5 \times 10^{-6}$ corresponds to the average distance between the dopant molecules $L_d \approx 100 \text{ nm}$. It means that chiral molecules in the distance of the order of $0.1 \mu\text{m}$ can induce a twist of the director of LC in a spiral. The mechanism of the formation of the macroscopic twist is not trivial because it requires initiation of a collective turn of a large number of LC molecules by an individual chiral molecule. As was noted in the introduction, there is no comprehensive microscopic theory of this effect. Therefore, we limit ourselves by a qualitative model only. Let us consider a chiral molecule in the nematic matrix. Angular interaction of the opposite sides of a chiral molecule with the nearest LC molecules is different. If this interaction is stronger than the interaction between LC molecules, the orientation of the long axes of LC molecules adjacent to opposite sides of the chiral molecule is also different introducing a chirality angle φ . Due to a long-range orientational interaction between LC molecules, these different orientations transmit into the LC on macroscopic distances. Since the neighboring chiral molecule is of the same sign of chirality, it induces the same sign of the twist deformation. Long-range orientational interaction of the nematic LC is described by a Poisson-like equation. Therefore, the twist deformations in a nematic matrix from all chiral molecules are linearly summed. As a result, a macroscopic director spiral with a pitch p , inversely proportional to the concentration of the dopant, appears, and this dependence is conserved for arbitrarily small concentrations of the dopant. The relationship between the pitch p and the chirality angle φ can be estimated as $pc_{\text{ch}} \approx \frac{2\pi l_{\text{LC}}}{\varphi}$, where l_{LC} is the distance between LC molecules. Substituting into this formula the

experimental numbers, $p = 3.5$ cm, $c_{\text{ch}} = 2.5 \times 10^{-6}$ and taken the distance between LC molecules $l_{\text{LC}} = 2$ nm, one can get the molecular chirality angle of the order of $\varphi \approx 0.1$ rad.

This model suggests that the LC host is composed of completely achiral molecules. However, many of LC molecules has no mirror symmetry. For example, the popular nematic LC 5CB, because of its twist around the bond connecting the two benzene rings, exists as two rapidly interconverting enantiomers. We suggest that, in addition to the described mechanism, chiral molecules can shift the equilibrium between the LC molecules enantiomers. In this case, a cholesteric spiral is caused by dopant-induced chiral interaction in the LC molecules.

In conclusion, the applied method of the measurement of the chiral pitch by measuring the orientation of the disclination

line allowed us to prove the linearity of the dependence $p^{-1}(c)$ in a wide-range of the pitches, extending from micrometers up to several centimeters. Such behavior of the pitch suggests that the formation of the chiral spiral in a nematic LC doped with chiral dopants can be described by long-range orientation distortions that are produced by short-range chiral interactions in the vicinity of the chiral molecules.

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