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Untwisting of the Helical Structure of Cholesteric Droplets with Homeotropic Surface Anchoring

M. N. Krakhalev[a, b]*, A. P. Gardymova[b], A. V. Emel'yanenko[c], Jui-Hsiang Liu[d], and V. Ya. Zyryanov[a]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,*
Krasnoyarsk, 660036 Russia

[b] *Institute of Engineering Physics and Radio Electronics, Siberian Federal University,*
Krasnoyarsk, 660041 Russia

[c] *Faculty of Physics, Moscow State University, Moscow, 119991 Russia*

[d] *Department of Chemical Engineering, National Cheng Kung University, 70101 Tainan, Taiwan*

* e-mail: kmn@iph.krasn.ru

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Cholesteric droplets dispersed in a polymer with homeotropic surface anchoring are studied. A director configuration with the bipolar distribution of the axis of the helix is formed in droplets. The untwisting of the helical structure (i.e., an increase in the pitch of the helix) is experimentally observed at a decrease in the size of droplets. This dependence is analyzed for liquid crystal droplets with various concentrations of the chiral addition. A proposed empirical relation describes well the correlation of the helix pitch and the size of droplets in the studied samples.

1. Chiral liquid crystals are of great scientific and technological interest. They are used as model objects for experimental studies of topological properties in the fields of physics [1−3], biophysics [4], and materials science [5]. Droplets of chiral liquid crystals have unique orientational structure, optical, and other properties because of the combination of a closed surface and the tendency of the director **n** (unit vector directed along the preferable orientation of long axes of molecules of liquid crystals) to form a twisted structure [6−13]. Recently, chiral liquid crystal droplets, in particular, chiral nematics (cholesteric liquid crystals), have been widely used in various fields of materials science. For example, in optics and photonics, cholesteric liquid crystal droplets were used as cavities for creating microlasers [14, 15], as well as photomechanical [16] and thermomechanical devices [17]. The optical and dielectric properties of cholesteric liquid crystals and their response to external actions depend on the configuration of the director **n** implemented inside droplets [18], which is in turn determined by boundary conditions (orientation of the director at the boundary of droplets), material parameters of cholesteric liquid crystals, and the relation of the pitch of the helix of cholesteric liquid crystals p_0 and the size of droplets d. In particular, in the case of tangential boundary conditions, a twisted bipolar configuration, a structure with a radial defect, and a transient structure are formed in cholesteric liquid crystal droplets at

$d/p_0 < 1.5$, $d/p_0 > 3$, and intermediate ratio, respectively [19].

The pitch of the helix and, therefore, the characteristics of cholesteric liquid crystals can be controlled by the temperature [8, 20, 21], optical radiation [22], and electric (magnetic) field [21, 23]. The parameters of the response (e.g., the threshold field) are determined by, in particular, the pitch of the helix p in the initial state, which does not generally coincide with the pitch of the helix p_0 observed in a bulk cholesteric liquid crystal (intrinsic pitch of the helix). This difference is due to the effect of boundary surfaces on which the director **n** has a given orientation. For example, in a planar cell with homeotropic boundary conditions (the director **n** is perpendicular to the interface), which is filled with a cholesteric layer with the thickness L, the helix of cholesteric liquid crystals is untwisted at the ratio $L/p_0 < 1$ and a homogeneous nematic structure occurs [24, 25]. At $L/p_0 > 1$, a twisted configuration of the director is formed but the pitch of the helix p is larger than the intrinsic pitch of the helix p_0 and depends on the thickness of the layer L [24−27]. A similar effect of the untwisting of the helix is observed in cylindrical cavities [28−30]; in this case, the difference of the pitch of the helix from the intrinsic pitch has a complex, sometimes nonmonotonic dependence [29, 30].
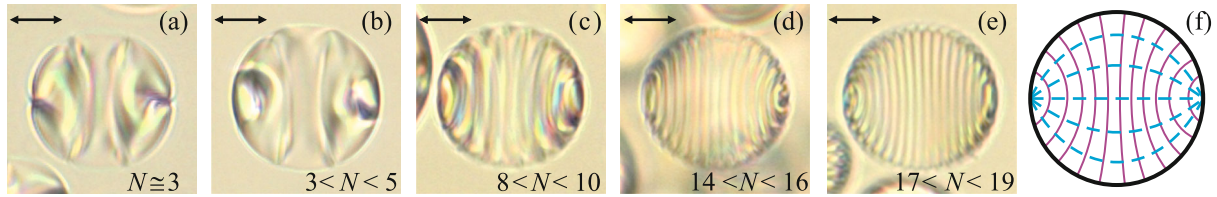
Fig. 1. (Color online) Photographs of cholesteric liquid crystal droplets with the sizes of (a) 17 and (b−e) 18−19 μm taken without the analyzer for the concentrations C = (a, b) 3.0, (c) 4.5, (d) 6.7, and (e) 7.7%, where N is the number of intervals between the optical texture lines, and the double arrows indicate the orientation of the polarizer. (f) Schematic of the structure with the bipolar distribution of the axis of cholesteric liquid crystals for $N \approx 12$. The distance between the solid lines corresponds to half the pitch of the helix. The dashed lines show the orientation of the axis of the helix in various regions of the droplet.

The effect of surface anchoring on pitch of the helix in cholesteric liquid crystal droplets is insufficiently studied. In particular, it was shown in [10] that the pitch of the helix in the structure with a radial defect is close to the intrinsic pitch of the helix p_0. In cholesteric liquid crystal droplets with weak anchoring, e.g., in droplet-like nuclei of a thermotropic cholesteric, which appear at the cooling of the isotropic phase, the twisted structure is undeformed with the pitch of the helix p_0 [17]. By analogy with a planar layer [24, 25], it is possible to assume that the interface in droplets with strong homeotropic anchoring can significantly affect the pitch of the helix. However, the chirality of the structure in such cholesteric liquid crystal droplets has not yet been analyzed. In particular, the authors of [12] mentioned that an untwisted radial structure is observed in droplets with $d/p_0 < 0.7$ and the authors of [31] showed that pitch of the helix in spheroidal inclusions of a cholesteric polymer liquid crystal in an isotropic polymer is 10% larger than that in a bulk chiral polymer liquid crystal. In this work, we study the chirality of the structure in cholesteric liquid crystal droplets with homeotropic anchoring.

2. We study a cholesteric liquid crystal based on E7 (Merck) nematic doped in cholesteryl acetate with concentrations C = 3.0, 4.5, 6.7, 7.7 wt %. The intrinsic pitch of the helix p_0 for all concentrations was measured by the droplet method [32]. The intrinsic pitch of the helix p_0 demonstrates a classical linear dependence on C^{-1} with the twisting power $\beta = 6.1$ μm^{-1}.

In order to obtain droplets with homeotropic anchoring, cholesteric liquid crystals were dispersed in poly(isobutyl methacrylate) (Sigma Aldrich), which specifies homeotropic boundary conditions for E7 nematic [33]. The composite film samples were fabricated by the TIPS technology [34] with the weight ratio cholesteric liquid crystal : poly(isobutyl methacrylate) = 60 : 40. The size of droplets d (visible diameter of droplets in the sample plane) was specified by the cooling rate and was in the range of 5−30 μm. The studies were performed with an Axio Imager.A1m (Carl Zeiss) polarization optical microscope at a temperature of t = 25°C.

The studied samples exhibit various optical textures, including droplets with periodically arranged lines (Fig. 1). Such droplets most often appear at the ratio $d/p_0 > 2.5$. The shape of the lines is close to a circular arc perpendicular to the boundary of the droplet, which corresponds to an orientational structure with a bipolar distribution of the axis of cholesteric liquid crystals [6, 35] characteristic of droplets with homeotropic anchoring. The observed lines correspond to the identical orientation of the director with respect to the observation direction in the central cross section of the droplet; consequently, the distance between the lines is equal to the distance at which the director is turned by π (half the pitch of the helix $p/2$). Consequently, such structures are convenient for the determination of the pitch of the helix in a droplet. It is noteworthy that the pitch of the helix depends on the position of the measurement point. For example, the pitch measured along the bipolar axis is smaller than the pitch of the helix measured near the equatorial region of the boundary. It is convenient to analyze the relative chirality parameter $N = 2d/p$ [9], which is the number of π-turns of the director along the bipolar axis. In the general case, N is not an integer, which complicates its estimate. For this reason, N is determined for the droplets, where the extreme texture lines reach the bipolar poles; in this case, N is an integer (Fig. 1a).

The dependence of N on d for all studied concentrations C of the chiral addition is nonlinear, $N < N_0 = 2d/p_0$, and the difference between N values increases with a decrease in the size of droplets d (Fig. 2). This means that the pitch of the helix p depends significantly on d.

Figure 3 shows the dependences of $N \cdot d$ on d^2. The analysis of the data provides the following expression for N:

$$N = a \cdot d - b/d. \qquad (1)$$

Here, the coefficient a can be determined from the condition that the second term becomes negligibly small at a sufficiently large size of droplets; i.e., the number of π-turns of the director on the diameter of
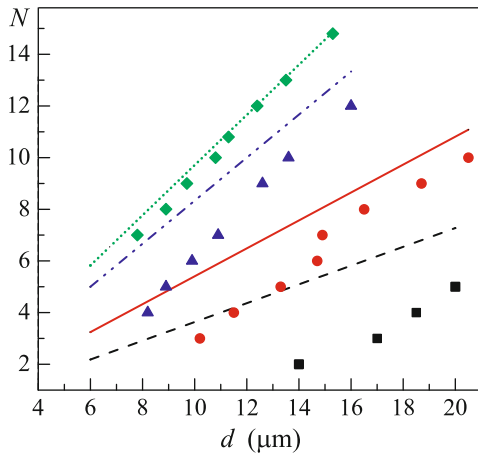
Fig. 2. (Color online) Experimental dependences $N(d)$ and dependences $N_0 = 2d/p_0$ for the concentrations of the chiral addition $C =$ (squares, dashed line) 3.0, (circles, solid line) 4.5, (triangles, dash-dot-dot line) 6.7, and (diamonds, dotted line) 7.7%.

Fig. 3. (Color online) Nd versus d^2 for the concentrations of the chiral addition $C =$ (squares) 3.0, (circles) 4.5, (triangles) 6.7, and (diamonds) 7.7% and the linear approximations of the corresponding experimental data.

droplets is specified by the intrinsic pitch of the helix: $N_0 = ad = 2d/p_0$; therefore, $a = 2/p_0$. This is in good agreement with the experiment according to the third and fourth columns of the table, where it is also seen that the coefficient b decreases monotonically with an increase in the concentration of the chiral addition (with a decrease in the intrinsic pitch of the helix p_0).

Expression (1) can be represented as

$$\frac{2\pi d}{p} = \frac{2\pi d}{p_0} - \frac{\pi b}{d}, \tag{2}$$

where $q = 2\pi/p$ is the magnitude of the wave vector along the bipolar axis of the cholesteric liquid crystal droplets. Then, Eq. (2) becomes

$$q = q_0 - \frac{\pi b}{d^2} = q_0\left(1 - \frac{\pi b}{q_0 d^2}\right). \tag{3}$$

It is noteworthy that a similar expression for the magnitude of the wave vector q_l in the planar layer of the cholesteric liquid crystal at homeotropic boundary conditions with the axis of the helix parallel to the substrate was obtained in [25]:

$$q_l = q_0\left(1 - \frac{|1 + 2\log(2qr)|}{4\gamma q_0 L}\right), \tag{4}$$

where $\gamma = K_2/K$, $K = K_1 = K_3$, K_i are the elasticity constants, r is the radius of the singular linear defect, and L is the thickness of the layer of the cholesteric liquid crystal. The comparison of Eqs. (3) and (4) shows that, with a decrease in the size of cholesteric liquid crystal droplets, q decreases (the pitch of the helix increases) more rapidly than the pitch of the helix q_l in the planar layer with comparable thickness. Dependences (3) and (4) on the size parameter are dif-
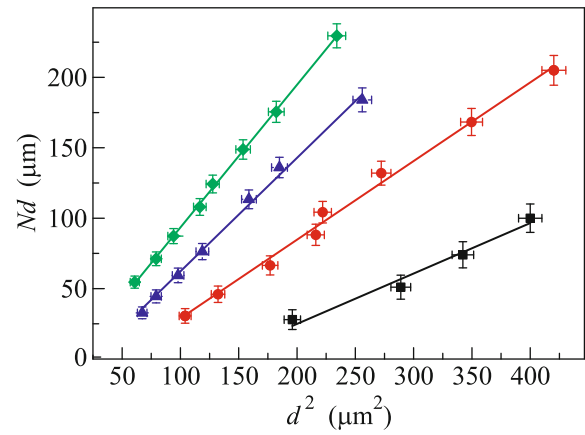
ferent because the orientational structure in the considered droplets has an axial symmetry and the boundary of droplets provides the untwisting effect on the helix of the cholesteric liquid crystal in two directions, whereas this effect in the planar layer occurs only in one direction.

3. Thus, the previous studies of the effect of boundary surfaces on the pitch of the cholesteric helix primarily concerned cholesteric liquid crystal layers and cylindrical capillaries [21, 24–30]. Similar phenomena could be expected and for cholesteric droplets with homeotropic anchoring. The experiments in this work certainly demonstrate the effect of untwisting of the cholesteric helix in droplets. The proposed empirical expression (1) approximates well the experimental dependences of the number of turns of the helix on the size of cholesteric liquid crystal droplets for all studied samples with various concentrations of the chiral addition. The results are important both for the analysis of topological structures in droplet ensembles of cholesteric liquid crystals and for the possible applications of cholesterics in various optoelectronic and photonic devices because the pitch of the helix is the most important structural parameter determining the

Intrinsic pitch of the helix p_0 at various concentrations C of the chiral addition and the coefficients a and b

C, %	p_0, μm	$2/p_0$, μm^{-1}	a, μm^{-1}	b, μm
3.0	5.5 ± 0.3	0.36 ± 0.02	0.36 ± 0.04	46.7 ± 12.9
4.5	3.7 ± 0.2	0.54 ± 0.03	0.56 ± 0.02	26.9 ± 5.2
6.7	2.4 ± 0.1	0.83 ± 0.04	0.81 ± 0.02	18.3 ± 3.9
7.7	2.0 ± 0.1	1.00 ± 0.05	1.01 ± 0.01	7.9 ± 1.7

optical and electro-optical characteristics of cholesteric liquid crystal cells.

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