Untwisting of a soft ferrocholesteric liquid crystal by shear flow and magnetic field

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Abstract. We theoretically study the effect of a shear flow and a uniform magnetic field on the helical structure of a ferrocholesteric liquid crystal with the finite anchoring between the liquid-crystalline matrix and magnetic particles (soft ferrocholesteric). The axis of the ferrocholesteric helix is orthogonal to the plane of the shear flow and the magnetic field. We derive the integral expressions for the pitch of the helix and magnetization of ferrocholesteric depending on the anchoring energy, field influence parameter, strength and orientation angle of the magnetic field, flow gradient and reactive parameter. It is shown that the shear flow is able to magnetize a ferrocholesteric liquid crystal. An increase in the field influence parameter or gradient of the shear flow velocity leads to a decrease in the critical fields of the ferrocholesteric-ferronematic transition.

1. Introduction

Cholesteric liquid crystals (CLC) have a spiral supramolecular structure the pitch of which is highly sensitive to external influences. Application of a magnetic field orthogonal to the axis of cholesteric helix with positive anisotropy of the magnetic susceptibility causes its untwisting [1]. Moreover, the flow of a liquid crystal with a velocity gradient leads to its orientation [2]. As shown in [3, 4], a shear flow can untwist the spiral structure of the cholesteric liquid crystal.

Doping of liquid crystals by nanoparticles of different nature leads to a significant modification of their physical properties, for example, an increase of birefringence and dielectric/magnetic anisotropy. So, the embedding of magnetic particles can reduce the magnetic fields necessary to control the orientation structure of liquid crystals. Such magnetic suspensions prepared on the basis of cholesteric liquid crystals are called ferrocholesterics (FCs) [5]. Combining the properties of ordinary isotropic liquids (fluidity) and crystals (anisotropy), FCs are highly sensitive to external fields. They demonstrate a variety of orientational and structural transitions. The influence of an external magnetic field on the orientational structure and magnetic properties of an FC has been studied in [6, 7, 8]. The possibility of controlling the spiral structure of an FC and its untwisting by a combined action of a magnetic field and a shear flow has been shown in [9].

In this paper, we examine the untwisting of helical structure of a ferrocholesteric liquid crystal under the action of a magnetic field and shear flow taking into account the finite anchoring between the subsystems.
2. Basic Equations

We consider a shear flow of unbounded ferrocholesteric with the velocity \( \mathbf{v} = [0, u(x), 0] \). The FC helical axis is perpendicular to the shear plane \( xOy \). The gradient of the velocity of the shear flow \( A = du(x)/dx \) is assumed to be constant over the whole FC sample. Shear flow leads to the aligning of LC molecules in the shear plane \( xOy \) at an angle \( \varphi_0 = 1/2 \arccos(-1/\lambda) \) [1] with respect to the direction of shear flow gradient. Here \( \lambda = -\gamma_2/\gamma_1 \) is the reactive parameter, \( \gamma_1 \) and \( \gamma_2 \) are the coefficients of the rotational viscosity of an LC.

The anchoring conditions between magnetic particles and an LC-matrix will be considered finite and planar, so in the absence of external fields the director \( \mathbf{n} \) of LC and the unit vector \( \mathbf{m} \) of FC magnetization are parallel to each other. We apply the magnetic field \( \mathbf{H} = H(\cos \varphi_H, \sin \varphi_H, 0) \) orthogonally to the axis of the ferrocholesteric helix in the shear plane \( xOy \) at some angle \( \varphi_H \). We assume the anisotropy of the diamagnetic susceptibility \( \chi_a \) of a liquid crystal to be positive, so both vectors \( \mathbf{n} \) and \( \mathbf{m} \) tend to orient along the field \( \mathbf{H} \).

In the considered geometry of the problem the magnetic field and the shear flow act competitively on the ferrocholesteric. Both mechanisms of influence orient the director of the ferrocholesteric in the plane \( xOy \) inducing the untwisting of its spiral structure. The vector fields \( \mathbf{n} \) and \( \mathbf{m} \) with such joint action of the magnetic field and the shear flow can be found in the form:

\[
\mathbf{n} = [\cos \varphi(z), \sin \varphi(z), 0], \\
\mathbf{m} = [\cos \psi(z), \sin \psi(z), 0].
\]  

(1)

The equations of motion of the director \( n_i \) [2] and the unit vector of magnetization \( m_i \) [10] are

\[
\gamma_1 \frac{dn_i}{dt} = -\frac{\delta F_V}{\delta n_i},
\]

(2)

\[
\gamma_{1p} f \frac{dm_i}{dt} = -\frac{\delta F_V}{\delta m_i},
\]

(3)

where \( \gamma_1 \) and \( \gamma_{1p} \) are the coefficients of the rotational viscosity of an LC and magnetic particles, respectively, \( d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla \) is the total time derivative, \( f \) is the volume fraction of magnetic particles. Variation of the free energy in Eqns. (2) – (3) is carried out under the additional conditions \( n_i^2 = 1 \) and \( m_i^2 = 1 \).

The bulk free-energy density of an FC in magnetic field for a finite anchoring between magnetic particles and CLC-matrix is written in the form [5, 11]:

\[
F_V = F_1 + F_2 + F_3 + F_4 + F_5,
\]

(4)

\[
F_1 = \frac{1}{2} [K_{11} (\nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n} + q_0)^2 + K_{33} (\mathbf{n} \times \nabla \times \mathbf{n})^2],
\]

\[
F_2 = -\frac{\chi_a}{2} (\mathbf{n} \cdot \mathbf{H})^2, \\
F_3 = -MS f \mathbf{m} \cdot \mathbf{H}, \\
F_4 = -\frac{w}{d} f (\mathbf{n} \cdot \mathbf{m})^2, \\
F_5 = \frac{k_B T}{v_p} f \ln f,
\]

where \( K_{11}, K_{22}, K_{33} \) are the Frank constants, \( q_0 > 0 \) is the wave number of the unperturbed spiral structure of an LC, \( M_S \) is the saturation magnetization of the magnetic particles material, \( v_p \) and \( d \) are the volume and the diameter of a magnetic particle, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( w \) is the surface energy density of anchoring between LC molecules and magnetic particles. We assume \( w > 0 \), i.e., in the absence of a magnetic field the free energy is minimal at parallel orientation of the director \( \mathbf{n} \) and the unit magnetization vector \( \mathbf{m} \), that corresponds to the so-called the planar anchoring between the director and the magnetization.
The concentration of magnetic particles is greater than some critical value \( f \) independent of the others. This is also an undesirable effect. As was shown in [5, 13], if the concentration of magnetic grains leads only to local director perturbations near each particle, magnetic particles due to the small volume fraction of admixtures. On the other hand, too low concentration of magnetic grains leads to the formation of large agglomerates of particles in the sample, which is an undesirable effect for FCs. In order to avoid this, the pair interaction potential of magnetic particles should be significantly less than thermal energy. For typical values of magnetic field effect on an FC, \( v_\psi \) characterizes the orientational distortions of the ideal particles solution to the free energy of a ferrocholesteric.

We consider the approximation of the homogeneous distribution of \( N \) magnetic particles with the constant volume fraction \( f(r) = \bar{f} \equiv N v_\psi / V \). Here \( \bar{f} \) is the average concentration of particles in the FC, \( v_\psi \) is the volume of a particle, and \( V \) is volume of the FC sample.

As is known, the dipole-dipole interaction between magnetic particles leads to their aggregation and the formation of large agglomerates of particles in the sample, which is an undesirable effect for FCs. In order to avoid this, the pair interaction potential of magnetic particles should be significantly less than thermal energy. For typical values of magnetic particle parameters and temperature of the LC phase we have [12] the following restriction on the volume fraction: \( f < 10^{-4} \). We neglect the magnetic dipole-dipole interactions between magnetic particles due to the small volume fraction of admixtures. On the other hand, too low concentration of magnetic grains leads only to local director perturbations near each particle, independent of the others. This is also an undesirable effect. As was shown in [5, 13], if the concentration of magnetic particles is greater than some critical value \( f_c \approx 10^{-8} \) for a sample with a characteristic linear size \( L \approx 10^{-2} \) cm), then the distortions of the orientation structure introduced by the particles overlap each other, covering already the entire volume of the sample. The system implements the so-called collective behavior, which provides a strong orientational anchoring between the anisometric magnetic particles and the LC-matrix. In this paper, we consider a suspension of magnetic particles, which satisfies the above requirements.

The bulk free-energy density \( F_V \) (4) for the considered geometry (see Eq. (1)) reads

\[
F_V = \frac{K_{22}}{2} \left( \frac{d\varphi}{dz} - q_0 \right)^2 - \frac{\chi a H^2}{2} \cos^2(\varphi - \varphi_H)
- M_S \bar{f} H \cos(\psi - \varphi_H) - \frac{w_\psi \bar{f}}{d} \cos^2(\varphi - \psi) + \text{const}.
\]

The projections of Eqs. (2) – (3) on the coordinate axes give a closed system of dimensionless equations for the angles \( \varphi \) and \( \psi \):

\[
\frac{d^2\varphi}{dz^2} - \frac{h^2}{2} \sin 2(\varphi - \varphi_H) - \sigma \sin 2(\varphi - \psi) + \frac{u}{\lambda} \left( 1 + \frac{1}{\lambda} \right) \cos 2\varphi = 0,
(5)
\]

\[
\xi h \sin(\psi - \varphi_H) - \sigma \sin 2(\varphi - \psi) = 0.
(6)
\]

Due to the low concentration of magnetic particles, we neglect the term in Eq. (6) describing the orienting effect of the shear flow on the unit magnetization vector.

The following dimensionless quantities were introduced in Eqs. (5) – (6):

\[
\zeta = q_0 z, \quad \sigma = \frac{w_\psi \bar{f}}{dK_{22}q_0}, \quad \xi = \frac{M_S \bar{f}}{q_0 \sqrt{K_{22}} \chi a}, \quad h = \frac{H}{H_q}, \quad u = \frac{A}{A_0}, \quad \lambda = -\frac{\gamma_2}{\gamma_1}.
(7)
\]

Here \( \zeta \) is the dimensionless coordinate, \( \sigma \) is the dimensionless anchoring energy, \( h \) is the dimensionless magnetic field strength. For the unit of the magnetic field, we have chosen the value \( H_q = q_0 \sqrt{K_{22} \chi a} \), for which the diamagnetic \( F_2 \) and elastic \( F_1 \) contributions to the free energy \( F_V \) (4) are of the same order. The field \( H_q \) characterizes the orientational distortions of
the FC caused by the LC-matrix and it is simply related to the cholesteric-nematic transition field: $H_c = \pi H_q/2$ [1].

The quantity $\xi = H_q/H_d$ is the ratio of two characteristic magnetic fields. The field
$H_d = K_{22}q_0^2/M_s f$ is obtained from the comparison of the elastic $F_1$ and ferromagnetic $F_3$ contributions and characterizes the orientational distortions of the ferrocholesteric caused by magnetic particles. If $\xi < 1$, i.e., $H_q < H_d$, the dominant mechanism of the magnetic field effect on the orientation structure of the ferrocholesteric is the action on the liquid crystal subsystem (quadrupole mechanism). For $\xi > 1$, i.e., $H_q > H_d$ the main mechanism is the effect on the ferromagnetic subsystem (dipole mechanism).

The parameter $u$ determines the dimensionless value of the gradient of the shear flow velocity
$a_0 = K_{22}q_0^2/|\gamma_2|$ taken as the unit of measurement. Here, the coefficient of the cholesteric rotational viscosity $\gamma_2$ is taken as an absolute value, since it is negative in LC with rodlike molecules [1]. The reactive parameter $\lambda$ is the ratio of the coefficients of the liquid crystal rotational viscosity.

Assuming [14, 15] $\chi_a \approx 10^{-7}$, $H \approx 10^4$ Oe, $f \approx 10^{-5}$, $q_0 \approx 10^4$ cm$^{-1}$, $K_{22} \approx 10^{-7}$ dyn, $M_s \approx 10^2$ G, $w \approx 10^{-1}$ erg/cm$^2$, $\gamma_1, \gamma_2 \approx 10^{-1}$ P, $d \approx 10^{-5}$ cm, and $A \approx 1$ s$^{-1}$, we obtain the following estimations for dimensionless parameters (7): $\lambda \approx 1$, $h \approx 1$, $\sigma \approx 10^{-2}$, $\xi \approx 1$ and $u \approx 10^{-2}$.

Note that system of Eqns. (5) – (6) can be obtained an alternative way proposed in [3]. For this purpose we introduce the effective potential

$$F_{\text{ef}} = \frac{F_{\text{ef}}}{K_{22}q_0^2} = \frac{1}{2} \left( \frac{d\varphi}{d\zeta} - 1 \right)^2 - \frac{h^2}{2} \cos^2(\varphi - \varphi_H) - \xi h \cos(\psi - \varphi_H) - \sigma \cos^2(\varphi - \psi) - \frac{u}{2} \left( \sin \varphi \cos \varphi + \frac{\varphi}{\lambda} \right).$$

The Euler-Lagrange equations written for this potential $F_{\text{ef}}[\varphi(\zeta), \varphi'(\zeta), \psi(\zeta)]$ give system of equations (5) – (6), which determines the angles $\varphi$ and $\psi$ of director and magnetization orientation in the ferrocholesteric as functions of the field strength $h$ and the orientation angle of the magnetic field $\varphi_H$, the anchoring energy $\sigma$ between the magnetic and liquid-crystalline subsystems, the parameter of the magnetic field influence on the system $\xi$, the reactive parameter $\lambda$ and the intensity of the shear flow $u$.

### 3. Pitch of a ferrocholesteric helix

As is known, the cholesteric helix can be untwisted by a magnetic field [2] and shear flow [3]. In the first case, the director of an CLC in fields greater than the threshold of the cholesteric-nematic transition will be directed along the magnetic field at an angle $\varphi_H$. In the second case the shear flow orients the director at the angle $\varphi_0$.

Let us analyze the combined effect of a shear flow and a magnetic field on the spiral structure of a ferrocholesteric with finite and planar anchoring between the particles and the LC-matrix. When the intensity of the magnetic field and the shear gradient reaches the critical values $h_c$ and $u_c$, the ferrocholesteric helix is untwisted, inducing ferrocholesteric – ferronematic transition. In the untwisted (ferronematic) phase, the director and the magnetization vector are oriented at some angles $\varphi_c$ and $\psi_c$, depending on the strength $h$ and the orientation angle $\varphi_H$ of the magnetic field, shear flow gradient $u$ and the reactive parameter $\lambda$, as well as the anchoring energy $\sigma$ between the LC molecules and the impurity.

In the untwisted phase the angles $\varphi_c$ and $\psi_c$ do not depend on the coordinates, so system of Eqns. (5) – (6) for the ferrocholesteric – ferronematic transition can be written as follows

$$h_c^2 \sin 2(\varphi_c - \varphi_H) + 2\sigma \sin 2(\varphi_c - \psi_c) - u_c(1/\lambda + \cos 2\varphi_c) = 0,$$

$$\xi h_c \sin(\psi_c - \varphi_H) - \sigma \sin 2(\varphi_c - \psi_c) = 0,$$

$$h^2 \sin 2(\varphi_c - \varphi_H) + 2\sigma \sin 2(\varphi_c - \psi_c) - u(1/\lambda + \cos 2\varphi_c) = 0,$$

$$\xi h \sin(\psi_c - \varphi_H) - \sigma \sin 2(\varphi_c - \psi_c) = 0,$$
where \( h_c \) and \( u_c \) are the critical values of the field and the velocity gradient at which the FC helix is untwisted.

The first integral of Eq. (5) reads

\[
\frac{d\varphi}{d\zeta} = \pm \sqrt{R(\varphi, \psi)}, \quad R (\varphi, \psi) = k - h^2 \cos^2 (\varphi - \varphi_H) - u (\sin \varphi \cos \varphi + \varphi / \lambda) - 2\sigma \cos^2 (\varphi - \psi) - 2\xi h \cos (\psi - \varphi_H).
\] (11)

The possible direction of twisting of an FC helix is determined by selecting one of the signs in Eq. (11). The unperturbed structure (\( h = u = 0 \)) of a ferrocholesteric is described by the solution \( \varphi = \zeta = q_0 z \). We assume \( q_0 > 0 \), which corresponds to the upper sign in Eq. (11).

The integration constant \( k \) depends on \( h, \varphi_H, u, \lambda, \sigma \), and is equal to \( 1 + 2\sigma \) in the absence of magnetic field and shear flow.

Integration over the period \( p \) of the FC structure (pitch of an FC helix) corresponds to a change in the angle \( \varphi \) by \( 2\pi \), therefore, taking into account (11), we obtain

\[
p = \int_0^p d\zeta = \int_{\varphi_c - 2\pi}^{\varphi_c} \frac{d\varphi}{\sqrt{R(\varphi, \psi)}}.
\] (12)

The integration constant \( k \) can be found from the minimum of

\[
F_p = \frac{1}{p} \int_{\varphi_c - 2\pi}^{\varphi_c} \sqrt{R(\varphi, \psi)} d\varphi - \frac{2\pi}{p} + \frac{1 - k}{2},
\] (13)

where \( F_p \) is the dimensionless effective free energy per one pitch of the FC helix. Minimizing expression (13) over \( k \) taking into account relations (11) – (12), we obtain the equation defining the integration constant:

\[
\int_{\varphi_c - 2\pi}^{\varphi_c} \sqrt{R(\varphi, \psi)} d\varphi = 2\pi.
\] (14)

The critical value \( k_c \), corresponding to a ferrocholesteric-ferronematic transition, i.e., the state when the helix pitch diverges, can be obtained from (11) with condition \( d\varphi/d\zeta = 0 \). Substituting \( k_c \) into the Eqn. (14), we obtain the relation that defines with conditions (9) – (10) the critical values of \( u_c \) and \( h_c \). This relation together with Eqns. (9) – (12), (14) form a closed system of equations for determining the pitch \( p \) of an FC helix.

4. Magnetic properties of a ferrocholesteric

The application of a magnetic field and a shear flow leads to a distortion of the initial unperturbed structure of an FC, changing its magnetization \( \mathcal{M} = M_s f \mathbf{m} \). In our case \( f = \bar{f} \), therefore the reduced magnetization \( \mathbf{M} = \mathcal{M} / (M_s \bar{f}) \) is completely determined by the vector \( \mathbf{m} \).

The projection of the reduced magnetization on the field direction \( M_H = \cos (\psi - \varphi_H) \) as a function of \( \zeta \) coordinate are presented in figure 1.

For small shear \( u \) and field \( h \), the angles \( \varphi (\zeta) \) and \( \psi (\zeta) \) differ slightly from \( \zeta \), corresponding to the helicoidal structure of an FC. With an increase in the magnitude of the shear flow gradient \( u \) on the structure period \( p \) (helix pitch) a region with almost constant values of the orientation angles appears. This corresponds to the plateau region in the spatial dependence of the magnetization \( M_H (\zeta) \) (figure 1, \( u = 0.228 \)). With increasing shear gradient \( u \) the width of
Figure 1. The dependence of the magnetization $M_H$ on the reduced coordinate $\zeta / p$ for various values of shear flow gradient $u$ at $\varphi_H = \varphi_0$, $\lambda = 1.1$, $\xi = 1$, $\sigma = 1$, $h = 0.2$; here critical shear flow gradient $u_c = 0.229$.

this region increases and the spiral structure of the FC loses its helicoidal character. As a result of reorientation of the magnetic particles, the ferrocholesteric is magnetized.

The projection of the reduced magnetization $\mathbf{M}$ on the direction of the magnetic field $\mathbf{H}$, averaged over the period of the structure $p$, can be written as

$$\langle M_H \rangle = \frac{1}{p} \int_{\varphi_c}^{\varphi_c + 2\pi} R(\varphi, \psi)^{-1/2} \cos (\psi - \varphi_H) d\varphi. \quad (15)$$

The average magnetization $\langle M_H \rangle$ as a function of shear flow gradient $u$ is shown in figures 2 – 3. In the absence of a flow, the magnetic field partially untwists an FC spiral structure and induces a nonzero magnetization in the system (figures 2 – 3 at $u = 0$). The magnetization increases slowly in weak shear flow, but increases strongly when critical shear $u_c$ is approached, at which it becomes equal to one. Changing the mechanism of the magnetic field influence on the FC helix from the quadrupole (figure 2, $\xi = 0.2$) to the dipole one (figure 2, $\xi = 2$) significantly reduces the magnitude of the shear gradient necessary to untwist the helix. In this case, smaller shear gradients $u$ are required to achieve the specified magnetization value.

5. Conclusion

We have studied the untwisting of helical structure of a ferrocholesteric liquid crystal by combined action of a magnetic field and shear flow. The axis of the ferrocholesteric helix was oriented orthogonal to the plane of the shear flow and the magnetic field. The finite and planar anchoring between the liquid-crystalline matrix and magnetic particles was assumed. We have derived the integral expressions for the pitch of the helix and the averaged magnetization of ferrocholesteric depending on the anchoring energy, field influence parameter, strength and orientation angle of the magnetic field, flow gradient and reactive parameter. The application of shear flow in magnetic field leads to a distortion of the original unperturbed structure of an FC, changing its magnetization. The projection of the reduced magnetization on the field direction as a function of coordinate has been calculated. We have obtained the dependence of average magnetization along the field direction on the magnetic field strength and the magnitude of shear flow gradient. Our results show that the shear flow is able to untwist and magnetize an FC. An increase in the magnetic field or the field influence parameter leads to a decrease in the critical shear flow gradient of the ferrocholesteric – ferronematic transition.
Figure 2. The average magnetization $\langle M_H \rangle$ along the direction of the magnetic field $H$ as function of shear flow gradient $u$ at $\varphi_H = \varphi_0$, $\lambda = 1.1$, $h = 0.2$, $\sigma = 1$ and for various values of $\xi$.

Figure 3. The average magnetization $\langle M_H \rangle$ along the direction of the magnetic field $H$ as function of shear flow gradient $u$ at $\varphi_H = \varphi_0$, $\lambda = 1.1$, $\xi = 1$, $\sigma = 1$ and for various values of magnetic field $h$.

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