Wave-like concentration profiles of a diamagnetic admixture in a cholesteric liquid crystal

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Abstract. The behavior of the orientation structure of a suspension of diamagnetic particles based on a cholesteric liquid crystal in an external magnetic field is theoretically studied. The effects of magnetic segregation and rigid homeotropic coupling between the liquid crystal matrix and admixture diamagnetic particles are taken into account. Within the framework of the continuum approach, a system of equations for the orientation equilibrium of the suspension was obtained using standard variational procedures. In the limit of weak magnetic fields, analytical dependences describing the behavior of the director vector field and the distribution of the admixture concentration along the suspension helix are obtained. A significant influence of the anisotropy parameter of the diamagnetic susceptibility subsystems on the wave-like concentration profiles in the suspension was revealed.

1. Introduction
Liquid crystals (LC) are substances that have the properties of both ordinary liquids (fluidity) and solids (anisotropy) [1]. One of the main features characterizing LCs is the anisometry of its molecules, which leads to a long-range orientational order in the direction of the molecular axes, that is, unlike isotropic media; they are spontaneously oriented approximately parallel to each other. In addition, such a type of liquid crystal as cholesteric LC (CLC) exhibits additional twisting of molecules in the direction perpendicular to their long axes. The spiral orientation structure of CLC can be reversibly deformed under the influence of external force fields (magnetic or electric), which is actively used in various indicators and sensors. However, one of the topical trends in this area of soft condensed media is associated not only with pure LCs, but also with various composite media based on LCs [2–3]. The behavior of a liquid crystal with embedded particles can differ significantly from the behavior of a pure liquid crystal. This is due to the appearance of additional degrees of freedom in the system and to the sensitivity of the impurity phase to external fields, which is often greater than that of a liquid crystal. In the present work, we theoretically study the behavior of a chiral suspension of diamagnetic particles (e.g., carbon nanotubes) based on a cholesteric LC in an external magnetic field.
2. Free energy and equilibrium equations

Let us consider an unbounded sample of a chiral liquid-crystalline suspension with low volume fraction \( \epsilon \ll 1 \) of the diamagnetic admixture [4–5], which is placed in a magnetic field \( \mathbf{H} = (0, H, 0) \) perpendicular to the axis of the CLC helix (see Fig. 1). The coupling between the LC matrix and impurity diamagnetic particles will be considered rigid and homeotropic. The equilibrium orientation structure of this suspension is determined by the minimum of its total free energy

\[
F = \int F_V dV,
\]

where the bulk density of the free energy of the suspension in a magnetic field has the form [6–8]:

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

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

\[
F_2 = -\frac{1}{2} \chi_a (\mathbf{n} \cdot \mathbf{H})^2,
\]

\[
F_3 = -\frac{1}{2} \chi^p_a f (\mathbf{m} \cdot \mathbf{H})^2,
\]

\[
F_4 = k_B T \ln f.
\]

Here \( \mathbf{n} \) is a director of the CLC, \( K_{11}, K_{22}, K_{33} \) are the elastic constants of the CLC (Frank’s constants), \( q_0 \) is the wavenumber of the spiral structure of the CLC, \( \chi_a \) is the anisotropy of the diamagnetic susceptibility of the CLC matrix, \( \mathbf{m} \) is a director of the impurity subsystem of diamagnetic particles, \( \chi^p_a \) is an anisotropy of the diamagnetic susceptibility of impurity particles, \( f \) is a volume fraction of diamagnetic particles in suspension. The term \( F_1 \) is the free energy density of orientation-elastic deformations of the CLC director field, the contributions \( F_2 \) and \( F_3 \) describe the quadrupolar mechanisms of interaction of subsystems with the magnetic field \( \mathbf{H} \), \( F_4 \) is the contribution of the mixing entropy of the ideal diamagnetic particles solution.

![Figure 1. Geometry of the problem](image)

In the absence of an external magnetic field the directors \( \mathbf{n} \) and \( \mathbf{m} \) are uniformly distributed in the \( xy \)-plane of CLC sample, while they continuously vary from layer to layer, rotating around the \( z \)-axis of the cholesteric helix. The unperturbed pitch of this helix \( p_0 = 2\pi/q_0 \). Rigid homeotropic coupling between subsystems assumes that directors are oriented perpendicular to each other (\( \mathbf{n} \perp \mathbf{m} \)), and the angles of their orientations are equal (\( \varphi = \psi \)). The applied magnetic field \( \mathbf{H} \) deforms the orientational structure of
the suspension in the $xy$-plane orthogonal to the axis of the helix, making it possible to search for the director fields of the subsystems in the following form:

$$
\mathbf{n} = (\cos \varphi, \sin \varphi, 0), \quad \mathbf{m} = (-\sin \varphi, \cos \varphi, 0).
$$

(3)

Taking into account relations (3), the free energy of the suspension (1) in terms of dimensionless quantities takes the form:

$$
\frac{F}{K_{22} q_0^2} = \int_V \left[ \frac{1}{2} \left( \frac{d\varphi}{d\zeta} - 1 \right)^2 - \frac{h^2}{2} \left( \sin^2 \varphi + \gamma \frac{f}{f_0} \cos^2 \varphi \right) + \kappa \frac{f}{f_0} \ln f \right] dV,
$$

(4)

where $\zeta = q_0 z$ is the dimensionless coordinate, $h = H/q_0 \sqrt{\chi_a/K_{22}}$ is the dimensionless magnetic field strength, $\gamma = \chi^{(1)}_{\text{imp}}/\chi_a$ is the parameter that characterizes the ratio of the specific anisotropies of the diamagnetic susceptibilities of impurity particles and a cholesteric, $\kappa = k_0 T f_0/(\nu K_{22} q_0^2)$ is the segregation parameter [6], $f_0 = NV/v$ is the average volume fraction of impurity.

The minimization of free energy (4) over $\varphi(\zeta)$ and $\zeta$, taking into account the particle conservation law, gives the following system of equilibrium equations:

$$
\frac{\partial^2 \varphi}{\partial \zeta^2} + h^2 \left( 1 - \gamma \frac{f}{f_0} \right) \sin \varphi \cos \varphi = 0,
$$

(5)

$$
f = f_0 Q \exp \left\{ \frac{h^2 \gamma}{2\kappa} \cos^2 \varphi \right\},
$$

(6)

$$
Q^{-1} = p^{-1} \int_0^{\zeta} \exp \left\{ \frac{h^2 \gamma}{2\kappa} \cos^2 \varphi \right\} d\zeta.
$$

(7)

The equation (5) has the first integral:

$$
\frac{d\varphi}{d\zeta} = \sqrt{A}, \quad A = C - h^2 \sin^2 \varphi - 2\kappa Q \exp \left\{ \frac{h^2 \gamma}{2\kappa} \cos^2 \varphi \right\}
$$

(8)

where $C$ is the integration constant. Equations (6) – (8) allow finding the function $\varphi(\zeta)$ and the pitch $p$ of the helix:

$$
\zeta = \int_0^{\varphi(\zeta)} \frac{d\varphi}{\sqrt{A}}, \quad p = \int_0^{2\pi} \frac{d\varphi}{\sqrt{A}}.
$$

(9)

The constant $C$ (8) can be obtained by minimizing of the free energy (4) over $C$ and satisfies the equation:

$$
\int_0^{2\pi} \sqrt{A} d\varphi = 2\pi.
$$

(10)

Thus, the system of equations (5) – (10) describes the orientation and concentration behavior of the suspension of diamagnetic particles based on a cholesteric LC in a magnetic field, taking into account the segregation effect.
3. Wave-like concentration profiles of an impurity in a weak magnetic field

Let us study the effects of concentration redistribution of diamagnetic impurities in the spiral structure of the suspension. Transformation of Eq. (7) by passing to integration over the director rotation angle $\varphi$ using expression (8) leads to a more convenient expression for $K$:

$$\int_0^{2\pi} \left[ 1 - Q \exp \left( \frac{h^2 \gamma}{2\kappa} \cos^2 \varphi \right) \right] A^{-1/2} d\varphi = 0. \quad (11)$$

The numerical solution of equations (6), (9) – (11) makes it possible to obtain the spatial dependence of the volume fraction of diamagnetic particles. In the case of weak magnetic fields, this dependence can be obtained analytically in the form of a series in powers of the field $h$. For this, it is necessary to expand equations (6), (9) – (11) using the following expansion of the constants $C$ and $Q$:

$$C = C_0 + C_1 h^2 + C_2 h^4 + \cdots, \quad Q = Q_0 + Q_1 h^2 + Q_2 h^4 + \cdots. \quad (12)$$

Solving the resulting system of algebraic equations for unknown expansion constants (12), in the second order we obtain

$$C = 1 + 2\kappa + \frac{h^2}{2}, \quad Q = 1 - \frac{h^2 \gamma}{4\kappa}. \quad (13)$$

Thus, taking into account the solutions for $C$ and $Q$, the expression for $A$ (8) looks as follows:

$$A = 1 + 2\kappa + h^2 \left( \frac{1}{2} - \sin^2 \varphi \right) - 2\kappa \left( 1 - \frac{h^2 \gamma}{4\kappa} \right) \exp \left( \frac{h^2 \gamma}{2\kappa} \cos^2 \varphi \right). \quad (14)$$

Thus, the implicit dependence $\varphi(\zeta)$ determined by equation (9), taking into account the expression for $A$ (16), can be represented as

$$\zeta = \varphi \left[ 1 + \frac{h^4}{32} (1 - \gamma)^2 \right] - \frac{h^2}{8} (1 - \gamma) \sin 2\varphi + \frac{h^4}{256} \left[ 3\gamma^2 - 6\gamma + 3 + \frac{\gamma^2}{\kappa} \right] \sin 4\varphi. \quad (15)$$

The dependence of the director component $n_y = \cos \varphi$ on the spatial coordinate $\zeta$ is shown in Fig. 2. The dashed line shows the harmonic function that describes the behavior of the director of pure CLC without additional admixture. In the presence of an impurity with positive anisotropy, the rotation of the director becomes sharper and the pitch of the helix increases. A change in the sign of parameter $\gamma$ leads to a significant increase in the pitch of the helix and to a smoother rotation of the orientation structure.

![Figure 2. Dependence of the director component $n_y = \cos \varphi$ on the spatial coordinate $\zeta$ along the helix axis](image)
Using the expansion in the small field \( h \), one can analytically find the wave-like concentration distribution of the impurity (6):

\[
\frac{f}{f_0} = 1 + \frac{h^2 \gamma}{4\kappa} \cos 2\varphi + \frac{h^4 \gamma}{64\kappa} [\gamma \cos 4\varphi + 2\kappa(1 - \gamma)].
\] (16)

The dependence of the reduced volume fraction of diamagnetic particles (16) on the coordinate along the helix axis is shown in Figure 3. The dotted line here shows the concentration dependence on the coordinate in the absence of segregation \((\kappa \to \infty)\). In this case, the spatial distribution of embedded diamagnetic particles is homogenous. An increase in segregation has a different effect on a suspension with positive and negative anisotropy. In a situation where the parameter \( \gamma \) is positive, the concentration of particles in the suspension changes harmoniously. The deviation of the ratio \( f/f_0 \) from unity is the stronger, the stronger the segregation (and the smaller the parameter \( \kappa \), respectively). If the parameter \( \gamma \) is negative, when segregation is taken into account, the asymmetry of the concentration function with respect to unity is observed. It can be said that in a certain preferred direction of the helix in the \( xy \)-plane (Fig. 1), the concentration of impurity particles is noticeably higher than in the opposite direction. For positive and negative values of \( \gamma \), an increase in impurity segregation is associated with an increase in the amplitude of the deviation of the reduced concentration from unity.

The parameter \( \gamma \) has a significant effect on the behavior of a suspension in a magnetic field. The influence of variation of this parameter on the dependence of the concentration of impurity particles on the coordinate can be observed in Fig. 4. As can be seen from the figure, the absence of impurities determines a uniform distribution of concentration along the entire length of the suspension helix. As the parameter \( \gamma \) grows in the region of positive values of the parameter, the amplitude and the period of the oscillations increase. Negative values of the parameter \( \gamma \), in addition to increasing the pitch of the helix, also cause an explicit asymmetry of the function relative to unity.

**Figure 3.** Dependence of the reduced volume fraction of particles on the coordinate along the axis of the helix:

a) \( \gamma > 0 \), b) \( \gamma < 0 \). Variation of the segregation parameter \( \kappa \)
Figure 4. Dependence of the reduced volume fraction of particles on the coordinate along the axis of the helix. Variation of the parameter $\gamma$

4. Conclusions
We have proposed a continuum description of the suspension structure within the framework of the model free energy functional of a cholesteric LC containing a small fraction of diamagnetic particles. The case of rigid homeotropic anchoring between LC and diamagnetic particles was considered. We have theoretically studied the behavior of an CLC suspension in a weak external magnetic field, taking into account the segregation effects. Using the small parameter method, we have obtained analytical dependences for the director field and the concentration of the impurity particles along the axis of the suspension helix. We have revealed a significant effect of the anisotropy of the diamagnetic susceptibility subsystems on the wave-like concentration profiles in the suspension.

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