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Magnetic field induced transitions in soft compensated ferrocholesteric liquid crystals

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ABSTRACT

Within the continuum theory, we study the influence of a magnetic field on the orientational and magnetic properties of a helicoidal liquid-crystal ferrosuspension, the so-called ferrocholesteric. We consider the compensated ferrocholesterics with soft planar coupling of magnetic particles with a liquid crystal matrix. We show that under the influence of a magnetic field applied perpendicularly to the axis of the helical structure of a ferrocholesteric, the unwinding of the helical structure takes place, and the transition to the ferronematic phase occurs. We study the dependence of the phase transition field on the suspension material parameters. The behavior of the average magnetization and the pitch of the helical structure as a function of a magnetic field is studied. It is shown that at soft coupling of particles with a liquid crystal matrix, the magnetization vector and the director have different pitches of the spiral structure in an external magnetic field.

1. Introduction

Ferrocholesteric liquid crystals or ferrocholesterics (FC) are colloidal suspensions of magnetic nanoparticles embedded in a cholesteric liquid crystal (CLC). Such suspensions are of great practical and fundamental importance [1–18]. The interest in researching them is due to the following circumstances.

First of all, liquid crystals (LC) have spontaneous orientational order, which due to the orientational coupling of the embedded particles with LC molecules, leads to the orientation of anisometric particles in the ordered phase of the suspension. For these reasons, LC suspensions are characterized by the unique properties [1,3,15,16,19], which are not typical for pure LCs. In a FC there are two mechanisms of interaction with an external magnetic field, a dipole mechanism (the effect of the field on the magnetic moments of ferroparticles), and a quadrupole mechanism (the effect on the diamagnetic cholesteric matrix). These orientational mechanisms determine the behavior of a suspension in a magnetic field.

If a CLC with a helical supramolecular structure acts as a matrix, then the long axes of the particles turn out to be helicoidally twisted together with the director of the matrix. For this reason, FCs are a LC analogs of helicoidal ferromagnets, in which, unlike solid helicoidal ferromagnets, magnetic particles are not fixed in the lattice, but they can migrate to those regions of the FC, where the sum of their magnetic and orientational energies has a minimum (the segregation effect [1]).

Secondly, FCs have a high sensitivity to external influences. The introduction of a small concentration of nanoparticles into the CLC matrix leads to an increase in the magnetic susceptibility by three or four orders of magnitude. Ferrocholesterics are attractive for the capability with the help of weak external magnetic fields to change the helicity of the formed structure and, thus, easily modulate the spectral composition of the reflected light. Due to this, the spiral structure of a FC is untwisted in a relatively weak magnetic field applied perpendicularly to the axis of the helical structure, and a ferrocholesteric–ferronematic phase transition occurs.

The possibility of existence of liquid-crystalline magnetic suspensions was theoretically predicted by Brochard and de Gennes [1], however, attempts at experimental realization of such media for a long time did not yield positive results: the suspensions were unstable and stratified into solid and LC phases. Modern experimental studies contain a lot of data on the successful synthesis of liquid-crystalline magnetic suspensions ([9,10,12-14,17,18,20-26]).

The response of LC suspension to the applied magnetic field depends strongly on the nature of orientational coupling and the coupling energy of the dispersed particles with the matrix. The case of strong coupling between the particles and the CLC matrix in compensated ferrocholesterics was studied theoretically for planar [15] and homeotropic [16] types of coupling. In this work we study phase transitions induced by a magnetic field in compensated

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ferrocholesterics with soft planar coupling of magnetic nanoparticles with a CLC matrix.

2. Free energy and basic equations

Let us consider the orientational and magnetic properties of a FC with soft planar coupling between ferroparticles and CLC molecules, i.e., we assume that the magnetic particles are embedded in the CLC matrix in such a way that in the absence of a field their main axes are oriented along the local director **n** (planar coupling), and the energy of interaction between the particles and CLC is finite (soft coupling). Let a magnetic field is directed perpendicularly to the axis of the helical structure of a FC, and the anisotropy of the diamagnetic susceptibility χ_a of the matrix is positive, then the director and the magnetic moments of the elongated particles tend to rotate in the direction of a field, i.e. both mechanisms of the magnetic field action on the suspension enhance each other and lead to the unwinding of FC spiral structure.

Depending on the method of preparation, liquid crystalline suspensions of anisometric magnetic particles may be magnetized or compensated [1,27]. In magnetized suspensions, the magnetic moments of the ferroparticles are coaligned at each point of the sample. If these suspensions are fabricated on the basis of CLC, they possess a helical structure and are liquid crystalline analogs of a helicoidal ferromagnets. Their magnetic susceptibility is much higher than in pure cholesterics [3–6]. Due to this, and also due to the orientational coupling of anisometric particles with an ordered cholesteric matrix, the reorientation fields decrease by two orders of magnitude in comparison with pure CLCs. In compensated FCs, in each quasinematic layer there are equal fractions of the magnetic impurity with oppositely oriented magnetic moments, so that in the absence of a magnetic field the compensated FC is a liquid crystalline analog of a helicoidal antiferromagnet [15,16].

The distortion of orientational structure of a FC caused by the magnetic field can be studied in the framework of continuum theory based on the free energy functional $\mathcal{F} = \int F dV$, where the free energy density F has the form [1,15,19]:

$$F = F_1 + F_2 + F_3 + F_4 + F_5, \tag{1}$$

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

$$F_2 = -\frac{\chi_a}{2}(\mathbf{nH})^2, \tag{3}$$

$$F_3 = -M_s(f_+ - f_-)\mathbf{mH}, \tag{4}$$

$$F_4 = \frac{k_BT}{\upsilon}\,(f_+\,\ln f_+ + f_-\,\ln f_-)\,, \tag{5}$$

$$F_5 = -\frac{W}{d}\,(f_+ + f_-)\,(\mathbf{nm})^2. \tag{6}$$

Here K_{11}, K_{22}, K_{33} are the Frank constants, q_0 is intrinsic wave number of the CLC helical structure, $p_0 = 2\pi/q_0$ is the helix pitch in the absence of a field, $\chi_a = \chi_\parallel - \chi_\perp > 0$ is the anisotropy of the CLC diamagnetic susceptibility, M_s is the saturation magnetization of the magnetic particles material, υ is the particle volume, d is its transverse diameter, f_+ and f_- are the volume fractions of magnetic particles with magnetic moments $\boldsymbol{\mu}_+ = M_s\upsilon\mathbf{m}_+$ and $\boldsymbol{\mu}_- = M_s\upsilon\mathbf{m}$, directed in the field absence parallel ($\mathbf{m}_+ \equiv \mathbf{n}$) and antiparallel ($\mathbf{m}_- \equiv -\mathbf{n}$) to the local director, **m** is a unit magnetization vector, W is the surface energy density of the orientational coupling of a CLC with magnetic particles, k_B iz Boltzmann constant, and T is a temperature.

In Eq. (1) the term F_1 is the bulk density of the energy of orientational-elastic deformations of the director **n**, the contribution F_2 is the density of the interaction energy of the diamagnetic liquid crystal matrix with the magnetic field **H**, the term F_3 corresponds to the interaction energy of the magnetic moments of the particles with the field [27], F_4 is a contribution of the mixing entropy of an ideal solution of particles in the free energy [1]. The last term F_5 is the energy density of the surface orientational interaction of magnetic particles with the LC matrix [19], which determines the orientational coupling of the magnetic and liquid crystal subsystems of the suspension. The finite values of $W > 0$ correspond to soft planar coupling of particles with the matrix; in this case $\mathbf{m} \parallel \mathbf{n}$ in the absence of a field.

We assume that the average fraction of magnetic particles in the suspension is small ($f_0 = N\upsilon/V \ll 1$), so the magnetic dipole-dipole interactions of the particles can be neglected (here N is the number of impurity particles, V is the volume of the suspension).

Due to the spiral structure of the CLC matrix and orientational coupling between the long axes of anisometric particles and CLC molecules, the magnetization vector $\mathcal{M} = M_s(f_+ - f_-)\mathbf{m}$ of a suspension is twisted in space. We choose the z axis as the axis of a FC helix and direct the magnetic field $\mathbf{H} = (0, H, 0)$ along the y axis. In this case, the vectors **n** and **m** lie in the (x, y) plane. Under the influence of an external magnetic field perpendicular to the axis of the FC helix, the orientational structure loses its helicoidal character, and the dependence of the components of the director and the magnetization on the coordinate z becomes non-harmonic:

$$\mathbf{n} = [\cos\varphi(z,H), \sin\varphi(z,H), 0]\,,$$
$$\mathbf{m} = [\cos\psi(z,H), \sin\psi(z,H), 0]\,. \tag{7}$$

Here $\varphi(z,H)$ and $\psi(z,H)$ are the angles of the director and the magnetization rotation, measured from the x axis respectively.

After the substitution of Eq. (7) into the free energy density (1) one obtains

$$F = \frac{K_{22}}{2}\left(\frac{d\varphi}{dz} - q_0\right)^2 - \frac{\chi_a H^2}{2}\sin^2\varphi - M_s\,(f_+ - f_-)\,H\sin\psi$$
$$-\frac{W}{d}\,(f_+ + f_-)\cos^2(\varphi - \psi) + \frac{k_BT}{\upsilon}\,(f_+\ln f_+ + f_-\ln f_-)\,. \tag{8}$$

It is convenient to rewrite Eq. (8) in a dimensionless form. We choose the quantity q_0^{-1} as a unit of length (then the dimensionless coordinate $\tilde{z} = q_0 z$) and introduce the notations for the dimensionless quantities [4,5]

$$h = \frac{H}{H_q}, \quad \xi \equiv \frac{M_s f_0}{q_0\sqrt{K_{22}\chi_a}}, \quad \kappa \equiv \frac{k_BTf_0}{\upsilon K_{22}q_0^2}, \quad \sigma \equiv \frac{Wf_0}{K_{22}q_0^2 d}. \tag{9}$$

Here h is the dimensionless field strength measured in units of the critical field $H_q = q_0\sqrt{K_{22}/\chi_a}$ of the cholesteric-nematic transition in a pure CLC [28]. The characteristic field H_q can be estimated from the balance of the terms F_1 (the twist energy density) and F_2 (the diamagnetic energy density) in Eq. (1): $K_{22}q_0^2 \approx \chi_a H_q^2$ (note that the exact result for the critical field in a pure cholesteric [28] is $\pi H_q/2$). For a FC the field H of the order H_q corresponds to the field of the ferrocholesteric-ferronematic transition if the quadrupole (diamagnetic) mechanism of the field effect on the FC predominates over the dipole (ferromagnetic) mechanism. Along with H_q we can define one more typical field. If a predominantly dipole mechanism is responsible for the ferrocholesteric-ferronematic transition, the elastic (F_1) and the dipole (F_3) contributions to the free energy turn out to be of the same order ($K_{22}q_0^2 \approx M_s f_0 H_d$) for $H = H_d$, where $H_d = K_{22}q_0^2/(M_s f_0)$. The field H_d corresponds to the ferrocholesteric-ferronematic transition field if the dipole mechanism dominates over the quadrupole one [1]. The parameter $\xi = H_q/H_d$ characterizes the

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