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Orientational bistability and magneto-optical response in compensated ferronematic liquid crystals

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ABSTRACT

In the framework of continuum theory we consider magnetic field induced transitions in soft compensated ferronematic liquid crystals, i.e., suspensions of ferromagnetic nanoparticles in nematic solvents with equiprobable distribution of the particles parallel and antiparallel to the director. Such systems are liquid-crystalline analogs of antiferromagnetics. We study the sequence of re-entrant transitions (uniform compensated phase – non-uniform phase – uniform saturation phase – non-uniform phase) between phases with different orientations of the director and magnetization. These transitions take place under the magnetic field action in the case of weak coupling between disperse magnetic phase and nematic matrix. We show that these transitions can be first or second order, and obtain the expressions for determining the order of orientational transitions. For the case of first order transitions, when the ferronematic shows orientational bistability, we study magnetic field influence on the orientational behavior of the director and magnetization, redistribution of magnetic impurity, and magneto-optical response.

1. Introduction

Colloidal dispersions of nanoparticles in liquid crystals (LC) are of great scientific interest as they successfully combine the ability of LC to self-aligning and physical properties of disperse particles which are absent in pure liquid crystals [1]. Addition of particles causes orientational distortions of the anisotropic liquid crystal medium that leads to interaction between particles which is not observed in isotropic matrices. This interaction depends on the nature of particles, properties of a LC and character of LC alignment on particle surfaces. Experimental investigations of liquid crystalline suspensions show that their optical properties are very sensitive to the presence of nanoparticles. Liquid crystalline suspensions of ferromagnetic or ferroelectric particles are of particular interest as their dipolar nature can decrease the control field and increase the orientational order due to interactions between nanoparticles and the LC matrix [1–12]. Thus, those dispersions essentially modify and improve physical properties of the LC matrix necessary for development of various devices and optical modulators. Almost in all the cases new applications of liquid crystal suspensions essentially depend on their ability to control an orientational response and spatial particle distribution in the LC matrix. A particular feature of liquid crystal suspensions of dipole nanoparticles is the effect of disperse phase segregation, consisting in the phenomenon of their accumulation in those areas of a sample where the sum of their energy in the external field and energy of orientational interaction with the matrix is minimal [13]. The segregation of particles results in concentrational inhomogeneity of the suspension that influences operational parameters of devices with this sort of anisotropic liquid as a working medium.

Apparently, the historically first examples of composite liquid crystal materials [13] are ferronematics (FN) which represent suspensions of anisometric ferro- or ferrimagnetic particles in nematic liquid crystals (NLC). The remarkable physics of these soft condensed media is conditioned by the mutual influence of anisotropic properties of spontaneously ordered LC media and prolate or oblate particles of a solid phase introduced into it, and also by two different mechanisms of magnetic field effect on their orientational structure. The first of them is usual for liquid crystals and is caused by anisotropy of diamagnetic susceptibility of the LC matrix, another one is connected with dispersed ferromagnetic nanoparticles. Interacting with magnetic moments of particles, the magnetic field changes their orientation, and forces of coupling between particles and LC transfer mechanical rotation of particles to the LC matrix. Orientational coupling between subsystems leaves its mark on those mechanisms of interaction with the external field that generates new magneto-optical effects specific to ferronematics which are absent in each of a component separately, and are of great interest not only for fundamental material science, but are very

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attractive for practical applications. In particular, ferronematic liquid crystals show a big variety of orientational and structural transitions induced by external magnetic, electric and laser fields, including re-entrant and tricritical phenomena [14–24].

Depending on a method of preparation the FN can be in one of two states: magnetized or compensated. Magnetized suspensions are characterized by co-alignment of ferroparticle magnetic moments in each local point of the sample (liquid crystal analog of a ferromagnetic) therefore the magnetic susceptibility of the magnetized FN is significantly higher than those ones of pure nematic liquid crystals. Consequently, and also due to the strong orientational coupling of particles with the nematic matrix the FN reorientation fields decrease till tens and units of oersted, i.e. they become at least two orders less in comparison with pure nematic liquid crystals. Compensated ferronematics have equal fractions of magnetic impurity with oppositely oriented magnetic moments so that in the absence of a magnetic field these systems are not magnetized, i.e. the compensated FN represents a liquid crystal analog of an anti-ferromagnetic. Such systems are not investigated theoretically so far: all known investigations assume that a ferronematic possesses initial (spontaneous) magnetization. Meanwhile, if in the process of suspension preparation one does not take special measures for its forced magnetization then the FN will be in the compensated state. The behavior of the compensated FNs in a magnetic field (i.e. its magnetic, orientational and optical properties) can essentially differ from the behavior of the magnetized suspension. Such differences are shown in Refs. [25–27] where the theory of magnetic field induced orientational transitions in compensated ferronematics has been proposed.

In the present paper we study the possibility of changing the character of orientational transitions in the magnetic field from the second to the first order causing the optical bistability of the ferronematic, and its magneto-optical response to the applied field.

2. The continuum description of compensated ferronematics

We consider the *compensated* FN which in the absence of a magnetic field has equal fractions of impurity with magnetic moments aligned parallel and antiparallel to the director so that the FN is not magnetized in whole and represents an LC analog of antiferromagnetic. We consider FN in a plane-parallel cell with the thickness L. Let us direct the x axis of the Cartesian coordinate system parallel to the bounding plates, the z axis – perpendicular to them; the origin of coordinates is in the layer center. We assume that the coupling between the director and the layer boundaries is absolutely rigid and planar, i.e. the director is fixed at the boundaries and its direction coincides with the easy orientation axis $\mathbf{e} = (1,\ 0,\ 0)$. We consider the coupling of magnetic particles with the LC matrix to be soft and planar so that in the absence of a magnetic field the alignment of the director and long axes of particles coincide. Let us direct the magnetic field $\mathbf{H} = (0,\ 0,\ H)$ perpendicular to the layer boundaries. The FN orientational structure deformation caused by the field influence we study within the framework of continuum approach, in which the free energy of the compensated FN is as follows [13,27]:

$$F = \iiint (F_1 + F_2 + F_3 + F_4 + F_5)\, dV, \tag{1}$$

$$F_1 = \frac{1}{2}\Big[K_1(\nabla\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_3(\mathbf{n}\times\nabla\times\mathbf{n})^2\Big],$$

$$F_2 = -\frac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2,\ F_3 = -M_s(f_+ - f_-)(\mathbf{m}\cdot\mathbf{H}),$$

$$F_4 = -\frac{w_p}{d}(f_+ + f_-)(\mathbf{n}\cdot\mathbf{m})^2,\ F_5 = \frac{k_BT}{v}(f_+ \ln f_+ + f_- \ln f_-).$$

here K_1, K_2, and K_3 are the Frank elastic modules; $\mathbf{n}$ is the liquid crystal director; $\mathbf{m}$ is the magnetization unit vector; M_s is the saturation magnetization of ferroparticle material; d is the transverse diameter of a particle; v is the particle volume, f_+ and f_- are volume fractions of particles with the magnetic moments $\boldsymbol{\mu}_+ = M_s v\,\mathbf{m}$ and $\boldsymbol{\mu}_- = -M_s v\,\mathbf{m}$, directed parallel and antiparallel to the local director $\mathbf{n}$ in the field absence, respectively; χ_a is the anisotropy of LC diamagnetic susceptibility (we assume $\chi_a > 0$, therefore the director tends to align along the field direction), w_p is the surface energy density of coupling between the magnetic particles and the director [24], k_B is the Boltzmann constant, T is the temperature. In the considered magneto-compensated suspension in the absence of a field $f_\pm \equiv \bar{f}/2$, where $\bar{f} = Nv/V$, N is the number of magnetic particles in the suspension, V is the FN volume. We assume $\bar{f} << 1$, that allows us to neglect interparticle magnetic dipole – dipole interactions in the suspension.

The first term (F_1) in equation (1) is the Oseen–Frank potential of orientationally elastic deformations of the director. The second and the third terms describe the interaction between diamagnetic LC matrix (F_2) and magnetic moments of the particles (F_3) with the external magnetic field, respectively. The fourth contribution (F_4) represents the finite energy of coupling between the magnetic particles and the LC matrix [28]; and the fifth term (F_5) describes the contribution of the entropy of mixing of the ideal solution of suspension particles. When $w_p > 0$, the energy F_5 is minimized at $\mathbf{m}\|\mathbf{n}$ that corresponds to the planar coupling of particles with the matrix.

To describe the orientational behavior of particles with different initial orientation of their magnetic moments in the magnetic field we use one variable – the vector $\mathbf{m}$ [27]. This is due to the fact that interaction between anisometric particles and the LC matrix is conditioned by the anisometry of their shape, anisotropy of orientational elasticity and the character of interaction between dispersed particles and the matrix (i.e. type of coupling). This interaction has nonmagnetic nature and therefore is not connected with the magnetic moment direction inside a particle [13]. Under the field action the individual particles deviate from the initial direction of their preferred axes and cause the distortions of the LC matrix orientational structure at the distances exceeding their own sizes [13,29]. If the particles are far from each other and spheres of orientational distortions generated by each of them do not overlap, then the particles behave independently, causing around themselves weak perturbations of the matrix initial state. Orientational interaction occurs between particles if regions of these distortions overlap. In this case the distortions induced by an individual particle are transferred to neighboring particles, initiating their coordinated rotation. This multiparticle orientational effect which is essentially important for LC suspensions is called *collective behavior* [13]. Macroscopic (continuum) approach used in this paper is valid in the case of collective behavior. A specific feature of the compensated FN is the fact that “the closest neighbors” of the individual particle are particles of “other sort”, i.e. with the opposite direction of their magnetic moment. In this case the collective behavior implies [13,27–29] that the rotation of ferroparticles with different initial orientations of their magnetic moments can be only coordinated, i.e. it has to be described by one vector $\mathbf{m}$ for “+” and “−” magnetic subsystems. This circumstance in the considered model of compensated FN is reflected in the contributions F_3 and F_4 in the free energy (1).

In the considered geometry the deformation of the director and magnetization can be presented in the form

$$\mathbf{n} = [\cos\phi(z),\ 0,\ \sin\phi(z)],\quad \mathbf{m} = [\cos\psi(z),\ 0,\ \sin\psi(z)]; \tag{2}$$