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Weak coupling effects and re-entrant transitions in ferronematic liquid crystals

A.N. Zakhlevnykh *, D.A. Petrov

Physics of Phase Transitions Department, Perm State University, Bukirev St. 15, 614990 Perm, Russia

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ABSTRACT

In the framework of continuum theory we study the orientational and magnetooptical properties of ferronematics (i.e., colloidal suspensions of magnetic nanoparticles in nematic liquid crystals) with soft planar coupling of a disperse phase with a liquid crystal matrix in a magnetic field. It is shown that there is a threshold energy of coupling between the dispersed phase and the liquid crystal matrix, below which (weak coupling) ferronematic has a complex magnetooptical response to an applied magnetic field. We show that at weak coupling initially a uniform ferronematic structure under the field action undergoes the sequence of re-entrant transitions "uniform phase–non-uniform phase–uniform phase–non-uniform phase", which can be of the first or second order depending on a segregation parameter value. The tricritical value of the segregation parameter is found analytically as a function of the material parameters of a suspension. We study magnetic field action on the optical phase lag and the capacity of a ferronematic cell. Comparison of results of numerical calculations with experimental data is carried out.

1. Introduction

Ferronematics (FNs) represent colloidal suspensions of prolate ferro- or ferriparticles in nematic liquid crystals [1,2]. Unlike usual liquid crystals (LCs), these complex liquids are highly sensitive to magnetic fields, and low concentration of impurity in general does not change the nature of orientational ordering of a liquid crystal matrix. The characteristic property of such a suspension is large magnetic susceptibility and the presence of orientational coupling between anisometric magnetic particles and liquid–crystalline matrix. This coupling causes two mechanisms of the magnetic field influence on the FN orientational structure: diamagnetic (the influence on the NLC-matrix) and ferromagnetic (the influence on the magnetic particles). These mechanisms lead to different orientational ordering of a FN in a magnetic field. In recent years there has been much interest in this field [2–26]. Experimental search goes in two directions: new mesogenic compounds (matrix), and new types of particles embedded in LC matrix, such as needle-like ferrite nanoparticles, nickel nanowires, and carbon nanotubes filled with ferromagnetic.

The first continuum theory of ferronematics was proposed by Brochard and de Gennes [1]. It considers the case of absolutely rigid planar coupling of prolate magnetic particles with an LC matrix, for which the director and magnetization are strictly parallel. Later it became clear that for real ferronematics the energy of coupling between the LC matrix and ferroparticles is finite, and Burylov and Raikher [27,28] proposed the model of soft ferronematics where the director and magnetization are independent variables. This theory formed a basis for further theoretical and experimental investigations of ferronematics (see Refs. [29,30] and review in Ref. [2]).

In this paper we study the orientational transitions induced by an external magnetic field in a FN plane layer with rigid planar coupling of a director at boundaries. The magnetic field is directed orthogonally to the plates bounding the layer, and the anisotropy of diamagnetic susceptibility of the liquid crystal is assumed positive (i.e. the LC director tends to be oriented along the magnetic field). Different aspects of this problem were investigated theoretically and experimentally by many authors. In Ref. [31] the case of absolutely rigid planar coupling between the director and magnetization of a ferronematic in the absence of the interaction of the diamagnetic nematic with an external magnetic field was considered in the framework of theory [1]. It is shown that the considered geometry corresponds to a non-threshold behavior of FN to the applied magnetic field, at that, with the increase of the field the deviations of the director and magnetization from the easy orientation axis on the boundaries of the cell monotonously increase and asymptotically tend to the magnetic field direction due to the rigid coupling of the director with the layer boundaries.

The case of soft planar coupling of the LC matrix with ferroparticles was considered in Refs. [32,33] within the framework of continuum theory [27,28]. The authors of Refs. [32,33] study orientational distortions of the director and concentrational distributions of ferroparticles depending on the applied magnetic field, layer thickness and energy

* Corresponding author. Tel.: +7 34223 96676; fax: +7 34223 96690.
E-mail address: anz@psu.ru (A.N. Zakhlevnykh).

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of coupling between the director and boundaries. They predicted the so-called *inversion transition* when due to the soft coupling between the LC matrix and the disperse phase with the increase of a magnetic field a detachment of the magnetization from the director occurs and the magnetic moments of ferroparticles are oriented along the field, and the director again becomes parallel to the easy orientation axis on the cell walls. In Refs. [34,35] the inverse Freedericksz effect is discussed in detail in a rather different geometry for the ferronematic with homeotropic coupling of the director on layer boundaries and on ferroparticle surfaces. This inversion orientational transition can be both of the first and second orders depending on the material parameters of the suspension. However, the authors of Refs. [32–35] did not take into account the magnetic field action on an LC matrix therefore with the field increase the director remains planar-oriented [32,33] in indefinitely strong fields and the results are valid for low or moderate fields.

In Ref. [6] this problem is considered in the absence of segregation while in Refs. [36–38] it is shown that the segregation of the magnetic admixture makes an essential contribution to the formation of distortions of orientational structure and leads to a tricritical behavior in external magnetic fields. Unlike in Refs. [32,33], threshold effects in strong magnetic fields are not investigated in Ref. [6] and inversion transitions are not discussed. In Refs. [6,39] a substantial enhancement in the FN magnetooptical response (as compared with the pure LC) even at low concentration of a disperse phase was experimentally observed.

In the present work we propose a consistent solution of the problem of a magnetic field action on a FN planar texture. Taking into account the segregation and diamagnetic effects we show that at *weak* coupling of disperse magnetic phase with the LC matrix the ferronematic has a complex response to the applied magnetic field, undergoing re-entrant “uniform phase–non-uniform phase–uniform phase–non-uniform phase” transitions. It is found that these transitions have a tricritical behavior. In the Conclusions, we compare the proposed theory with the experimental data.

2. Free energy of ferronematics and orientational equilibrium equations

We consider a planar ferronematic cell of thickness L. Let us introduce the rectangular coordinate system, align the x axis parallel to bounding plates, and the z axis — perpendicular to them and assume that the coordinate origin is in the layer center (see Fig. 1). We also assume that on the layer boundaries the alignment of the director is fixed and coincides with the easy orientation axis $\mathbf{e} = (1, 0, 0)$ [rigid planar coupling], and the coupling of ferroparticles with the director $\mathbf{n}$ is soft [i.e. it is characterized by the finite energy of orientational interaction

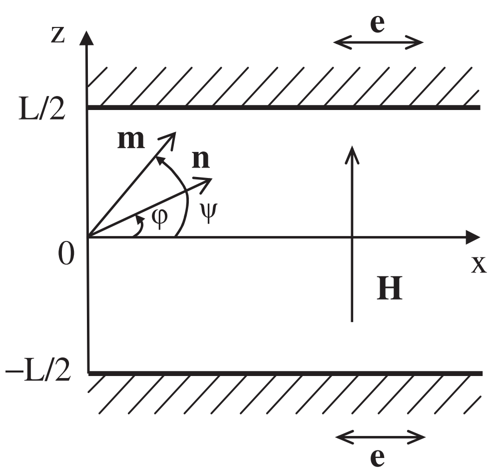

Fig. 1. The ferronematic planar layer in an external magnetic field.

w_p] and planar [i.e. in the field absence the long axes of magnetic particles are parallel to the director]. Let us align the magnetic field $\mathbf{H} = (0, 0, H)$ perpendicular to the layer boundaries.

We study distortions of the FN orientational structure within the framework of the continuum theory in which the FN free energy has the form

$$F = \iiint F_V dV \tag{1}$$

with the volume density of free energy of FN [27,28]

$$\begin{aligned} &F_V = F_{elast} + F_{diam} + F_{ferr} + F_{surf} + F_{entr},\\ &F_{elast} = \frac{1}{2}\left[K_1(\nabla\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_3(\mathbf{n}\times\nabla\times\mathbf{n})^2\right],\ F_{diam} = -\frac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2,\\ &F_{ferr} = -M_s f(\mathbf{m}\cdot\mathbf{H}),\quad F_{surf} = -\frac{w_p}{d} f(\mathbf{n}\cdot\mathbf{m})^2,\quad F_{entr} = \frac{k_B T}{v} f\ \ln f, \end{aligned} \tag{2}$$

where K_1, K_2, and K_3 are the Frank modules of LC orientational elasticity; $\mathbf{n}$ is the LC director; f is the volume fraction of particles with the magnetic moments $\boldsymbol{\mu} = M_s v\mathbf{m}$ aligned parallel to the local director $\mathbf{n}$ in the absence of a field; $\mathbf{m}$ is the unit vector of suspension magnetization; M_s is the saturation magnetization of the particle; χ_a is the anisotropy of diamagnetic susceptibility of a liquid crystal (we assume $\chi_a > 0$ therefore the director tends to rotate in the direction of a field); w_p is the density of surface energy of interaction between the particles and the LC matrix (we assume $w_p > 0$, in this case in the absence of a magnetic field the free energy F_{surf} is minimal at $\mathbf{n}\ \mathbf{m}$ that corresponds to the planar coupling between the director and magnetic particles); d is the transverse diameter of a particle; v is the particle volume; k_B is the Boltzmann constant; and T is the temperature. In the diluted suspension $\bar{f} = Nv/V \ll 1$ (here N is the number of magnetic particles in the suspension, V is the ferronematic volume) that allows us to neglect interparticle magnetic dipole–dipole interactions. The contribution F_{elast} in Eq. (2) represents the density of free energy of orientational elastic deformations of the director (Oseen–Frank potential). The second (F_{diam}) and third (F_{ferr}) ones characterize the interaction between the diamagnetic nematic and the magnetic moments of particles with the external magnetic field $\mathbf{H}$ respectively. The fourth term (F_{surf}) describes the energy of coupling between the NLC matrix and ferroparticles; the last contribution (F_{entr}) takes into account the mixing entropy of the ideal solution of suspension particles.

In the considered case (Fig. 1) the deformation of the FN orientational structure induced in the magnetic field corresponds to the combinations of splay and bend of the director and the solution can be found in the following form:

$$\mathbf{n} = [\cos\varphi(z), 0,\ \sin\varphi(z)],\quad \mathbf{m} = [\cos\psi(z), 0,\ \sin\psi(z)]; \tag{3}$$

where $\varphi(z)$ and $\psi(z)$ are the angles of deviation of the director and magnetization from the easy orientation axis $\mathbf{e} = (1, 0, 0)$, respectively. The choice of the angles and coordinate axes is presented in Fig. 1. According to Refs. [35,36] we introduce the dimensionless parameters

$$h = HL\sqrt{\frac{\chi_a}{K_1}},\ k = \frac{K_3}{K_1},\ g = \frac{f}{\bar{f}},\ \zeta = \frac{z}{L},\ b = \frac{M_s\bar{f}L}{\sqrt{K_1\chi_a}},\ \kappa = \frac{k_B T\bar{f}L^2}{K_1 v},\ \sigma = \frac{w_p\bar{f}L^2}{K_1 d}. \tag{4}$$

Here h is the dimensionless magnetic field strength; g is the reduced particle volume fraction in the suspension; ζ is the dimensionless coordinate; and k is the parameter of orientational elasticity anisotropy. The dimensionless parameter b is defined according to Ref. [36] and represents the ratio of two characteristic fields $b = H_q/H_d$. One of them, $H_q = L^{-1}\sqrt{K_1/\chi_a}$, which we use in Eq. (4) as a unit of field strength, characterizes the threshold field at which the distortions arise in the ferronematic orientational structure due to the quadrupole (diamagnetic) mechanism of the magnetic field action. The other,