Magnetically induced bistable behavior of ferronematic liquid crystals

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(Received 18 July 2013; published 22 November 2013)

In the framework of the modified model [S. V. Burylov and A. N. Zakhlevnykh, Phys. Rev. E **88**, 012511 (2013)] of soft ferronematic liquid crystals, i.e., suspensions of needlelike ferroparticles in nematic solvents, we consider the ferronematic states with different mutual orientations of the director and magnetization. We study the transitions between states in an external magnetic field and show that these transitions are characterized by either continuous or discontinuous changes in the order parameter; i.e., they can be both the second-order and the first-order, respectively. In the latter case the magnetic field induced orientational hysteresis arises, which can be observed in experiments on the birefringence of ferronematic liquid crystals.

DOI: 10.1103/PhysRevE.88.052503 PACS number(s): 61.30.Gd, 77.84.Nh, 64.70.M−, 42.70.Df

I. INTRODUCTION

Recently, in Ref. [1] we proposed a modified theory of soft ferronematic liquid crystals (FNs), i.e., suspensions of needle like ferri- or ferromagnetic particles in nematic liquid crystals (NLCs). The magnetic susceptibility of these suspensions is at least two orders of magnitude higher than that of pure NLCs [2–6]. Due to this, the orientational structure of FN can be controlled by relatively weak ($\leqslant$100 Oe) magnetic fields.

The proposed modified theory [1] is based on the development of the existing continuum approaches to the description of rigid [2] and soft [3] FNs and differs, mainly, in describing of the orientational interaction between the ensemble of ferroparticles and nematic matrix. The main stages of the construction of a continuum model of FNs, the description of the orientational interaction, i.e., a ferroparticles orientational energy, in existing theories [2] and [3], as well as the distinctive features of our modified approach, are as follows.

For the construction of the continuum model of FN two interconnected levels of theoretical consideration are used which differ in characteristic scales: mesoscopic and macroscopic. At the mesoscopic level with a typical scale of the order of the ferroparticle length L the behavior of an individual particle in a uniform nematic matrix is considered. Here the main problems are the theoretical description of local deformations of the director near the particle, determination of equilibrium orientation of the particle (i.e., its long axis) with respect to the unperturbed NLC director, and modeling of ferroparticle orientational energy at the deviation of the particle from its equilibrium under the action of an external magnetic field $\boldsymbol{H}$. At the macroscopic (or continuum) level the results of mesoscopic research are averaged at scales much greater than L, the collective orientational interaction between the ferroparticle ensemble and the nematic matrix is considered, and the expression for the volume density of FN free energy in the external magnetic field is derived. This expression is a basis for further theoretical studies of orientational and magnetic behavior of FN in samples with different geometries.

At the continuum level of theoretical consideration of FNs the director $\boldsymbol{n}(\boldsymbol{r})$ and the magnetization vector $\boldsymbol{M}(\boldsymbol{r})$ are used for the description of orientational order of nematic and magnetic subsystems, respectively. In the uniaxial liquid crystal matrix, the director $\boldsymbol{n}$ varies only in its direction. At the same time, the magnetization vector $\boldsymbol{M}$, which is the product of the volume fraction f of the solid phase on the saturation magnetization M_S of the particle material, and the unit vector $\boldsymbol{m} = (\boldsymbol{M}/M)$, i.e. $\boldsymbol{M} = fM_S\boldsymbol{m}$, can vary both in its direction and in magnitude. Therefore, for its determination it is necessary to find a distribution of the vector $\boldsymbol{m}(\boldsymbol{r})$ [$\boldsymbol{M}$ varies in direction] and a distribution of the local concentration $f(\boldsymbol{r})$ [$\boldsymbol{M}$ varies in magnitude]. Thus, the volume density of FN free energy must depend on three variables: $\boldsymbol{n}$, $\boldsymbol{m}$, and f.

From this viewpoint the first continuum model of FNs, proposed by Brochard and de Gennes in Ref. [2], looks too simplified. Solving mesoscopic problems, the authors of Ref. [2] used the approximation of rigid anchoring of nematic molecules at ferroparticles surfaces (the model of rigid FNs). They demonstrated that in the three most probable types of anchoring—longitudinal, homeotropic, and circular (see Refs. [1–3,7,8])—each individual particle is aligned strictly parallel to the unperturbed NLC director in the fields of about several tens of oersteds. At the macroscopic level it leads to the condition $\boldsymbol{m} = \boldsymbol{n}$ that limits the general consideration: The number of independent variables reduces from three to two in the volume density of FN free energy. Additionally, the continuum theory [2] of rigid FNs takes into account only the dipole mechanism of interaction between the ferroparticle ensemble and the external field. It can be used only at low ($H \sim$ 1–10 Oe) magnetic fields. At high fields ($H \geqslant 10^2$ Oe), when there is the quadrupole mechanism of interaction between the ferronematic and the external field caused by the diamagnetic anisotropy of the nematic matrix, the condition $\boldsymbol{m} = \boldsymbol{n}$ is not satisfied anymore and the theory [2] cannot be used for the description of orientational and magnetic behavior of FNs.

Developing the theoretical approach for description of ferronematic liquid crystals, Burylov and Raikher in Refs. [7,8] reconsidered the mesoscopic problems concerning the behavior of an individual particle in a nematic matrix. They studied the case of finite values of anchoring energy W of a nematic liquid crystal at the particle surface and theoretically

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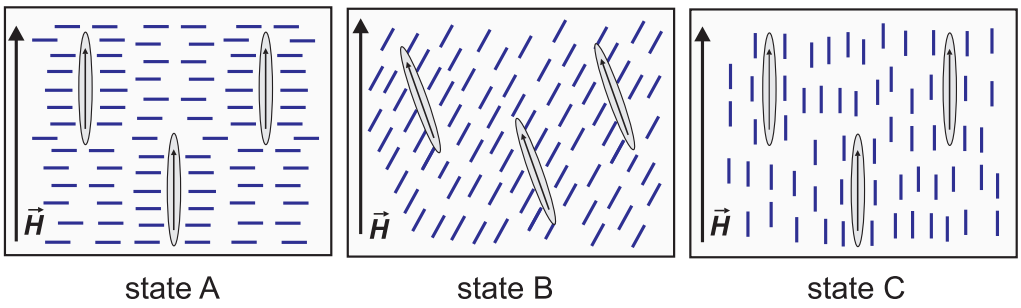

FIG. 1. (Color online) Orientational states of FN in an external magnetic field.

showed that depending on the type of anchoring and material parameters, in the absence of external field the particle can be oriented along or perpendicular to the director. An applied magnetic field induces rotation of the ferroparticle and its deviation from the initial equilibrium position. This deviation is characterized by the orientational energy, which the authors of Refs. [7,8] suggested to write in the form of quadratic contribution in $\cos\theta$, where θ is the angle between the direction of a long axis of the particle and the NLC director. In order to receive the macroscopic (continual) description of magnetic suspension, Burylov and Raikher [3] obtained the expression for the volume density of FN free energy in which the orientational energy of ferroparticle ensemble includes the quadratic contribution from the scalar product $(\boldsymbol{m}\cdot\boldsymbol{n})$,

$$F_{OR,2}(\theta) = A_2 f(\boldsymbol{m}\cdot\boldsymbol{n})^2. \tag{1}$$

Here, for the orientational energy and other parameters we use the notation of Ref. [1], where, in particular, it is shown that the coefficient A_2 in the model [3] can be expressed in terms of volume v of an individual ferroparticle and the difference in free energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ for parallel ($\mathcal{F}'_{\parallel}$) and perpendicular ($\mathcal{F}'_{\perp}$) orientation of the long axis of the particle with respect to the nematic director of the uniform nematic matrix, i.e.,

$$A_2 = \frac{\mathcal{F}'_{\parallel} - \mathcal{F}'_{\perp}}{v}. \tag{2}$$

The values of the energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ depend on the type of anchoring, i.e., on the boundary conditions for the director on the surface of the particle. For the calculation of these energies in Ref. [3] the approximation of soft anchoring (model of soft FNs) was used, which is valid for the magnetic suspensions with $w = (WR/K) \ll 1$, where R is the particle radius, K is the average of bulk elastic constants of NLC (splay K_{11}, twist K_{22}, and bend K_{33}). The condition $w \ll 1$ is satisfied, for example, in real thermotropic suspensions [4–6]. As a result, for the coefficient A_2 the following relationship was obtained:

$$A_2 \cong -2\frac{W}{d}P_2(\cos\alpha), \tag{3}$$

where $d = 2R$ is the particle diameter, $P_2(\cos\alpha) = (3\cos^2\alpha - 1)/2$ is the second-order Legendre polynomial, and α is the angle between the easy director orientation on the particle surface and the long axis of the particle. In comparison with the model [2], which corresponds to the rigid anchoring ($w \gg 1$), in the theory [3] of soft FNs the volume density of free energy depends on the full number of independent variables $(\boldsymbol{n},\boldsymbol{m},f)$ and additionally includes the diamagnetic contribution that allows one to use this theory for any range of field strength. In this approach, as shown in Ref. [9], a ferronematic liquid placed in an external magnetic field can have three states with various mutual orientation of the director and magnetization, i.e., with different values of the angle θ between $\boldsymbol{n}$ and $\boldsymbol{m}$: *homeotropic* (state A: $\theta = \pi/2$, $\boldsymbol{m}\perp\boldsymbol{n}$), *angular* (state B: $0 < \theta < \pi/2$), and *parallel* (state C: $\theta = 0$, $\boldsymbol{m}\parallel\boldsymbol{n}$); see Fig. 1. In an unbounded FN, the transitions between those states in a magnetic field have a threshold character and are the second-order transitions [9].

As to the restricted volumes, in particular, planar FN cells with different orientations of an external magnetic field with respect to the vectors $\boldsymbol{n}$ and $\boldsymbol{m}$, the theory [3] of soft FNs predicts that along with the transitions of the second order, also the first-order transitions between states can take place; see Refs. [10–16]. It is caused by the influence of cell walls which impact on the orientation of a nematic director in a cell. For FN cells with specific geometry, the conditions at which the second-order transitions between orientational states change to the first-order ones were determined in Refs. [11–16].

The theory [3] of soft FNs and its application [17–19] to the description of orientational behavior of real magnetic suspensions gave a proper explanation of experimental data that cannot be done using the model [2] of rigid FNs. However, if we consider the theory [3] of soft FNs critically, it should be noted that the form (1) of orientational energy in this model is the most simple one, which contains only the quadratic contribution in $(\boldsymbol{m}\cdot\boldsymbol{n})$. The result (3) of the calculation of A_2 is valid at $w \ll 1$ for cylindrical (rodlike, needlelike, or ellipsoidal) particles with $(L/d) \geqslant 10$. In calculations it makes it possible to neglect the existence of end effects and local deformations of the director near particles. In real FNs, the end effects and the local orientational distortions near particles play, of course, a certain role. As was shown in Ref. [2], the end effects can make corrections to the energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ and, as a result, to the coefficient A_2 : These corrections are proportional to the ratio of the end surface area $2S_E = (\pi d^2/2)$ to the side surface area $S_S = \pi dL$ of the cylinder, i.e., $(2S_E/S_S) \sim (d/L) \sim 10\%$. The correction of the same order at determination of A_2 in the model [3] can be made by considering the local deformations of the director field near side surfaces of ferroparticles (i.e., the second order in w in the expansion of energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ at the parallel and perpendicular orientation, respectively, of the particle with respect to the NLC director; see Eq. (18) in Ref. [1]). To the same number of corrections one can attribute the possible influence of the saddle-splay elastic constant K_{24} of NLC on the values of energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ and, therefore, on the estimate of the coefficient A_2. This effect has not been studied,

because in Refs. [2,3,7,8] the constant K_{24} is not taken into account. Additionally, the deviation of the particle shape from cylindrical (for example, ellipsoidal particles) also has to make the correction to this coefficient. The general consideration of these corrections and its proper description can influence on the quadratic type of orientational energy proposed by Burylov and Raikher. Therefore, in the development of their approach to the description of FNs the following major question was in front of us: How do effects of secondary importance influence the orientational energy of particles?

This question has been already discussed by a number of authors. In particular, Zadorozhny *et al*. [12,13] proposed to consider the coefficient A_2 in the model [3] of soft FNs as a phenomenological (fitting) parameter which must be obtained not from theoretical estimates, but from the analysis of experimental results. This procedure was approved in Refs. [20,21]. However, in our opinion, such modification of model [3] of soft FNs leads to a simple renormalization of anchoring energy W in the theoretical expression for A_2 from Eq. (3). We assume that by using one and the same surfactant for processing the particles of submicronic dimensions and flat surfaces the corresponding values of anchoring energy W may not coincide. Apparently, this fact and the influence of the corrections described above are implied in the approach of Zadorozhny *et al*. to the definition of the constant A_2. As for the general form of orientational energy of ferroparticles, in Refs. [12,13] it does not differ from the model [3] of soft FNs.

Another idea is suggested by Baldin and Zakhlevnykh in Ref. [22]. Considering magnetic suspensions with the homeotropic type of anchoring at ferroparticle surfaces, the authors of Ref. [22] proposed to take into account not only the second order in $(\boldsymbol{m}\cdot\boldsymbol{n})$ in the orientational energy, but also the fourth-order one. As the major argument for that modification, Baldin and Zakhlevnykh used the analogy with a more general (in comparison with the Rapini potential [23]) expression for the density of surface energy of nematic anchoring at a rigid substrate, which includes a term of this type (compare the surface energy of NLC in Refs. [23] and [24]). However, up to now this theoretical approach was not developed in the literature. The reasons are as follows. First, the suggested form of orientational energy breaks traditional ideas of the behavior of particles in the nematic matrix of FN since it allowed for the possibility of their bistable or tilted orientation with respect to the NLC director in the absence of an external magnetic field [1]. Second, the main idea of this modification is not supported by detailed theoretical justification, in particular, at the mesoscopic level.

In Ref. [1], we carried out the mesoscopic study for the anchoring of arbitrary type at the surface of a single particle. Going to the continuum (macroscopic) description of magnetic suspensions, we have shown that, in general, the orientational energy of the ensemble of ferroparticles is an infinite series in even powers of the scalar product $(\boldsymbol{m}\cdot\boldsymbol{n})$:

$$F_{OR}(\theta) = f\sum_{k=1}^{\infty} A_{2k}(\boldsymbol{m}\cdot\boldsymbol{n})^{2k}. \tag{4}$$

It was also found that for the sum of the coefficients A_{2k} in the expansion (4) more general expression than (2) takes place

$$\sum_{k=1}^{\infty} A_{2k} = \frac{\mathcal{F}'_{\parallel} - \mathcal{F}'_{\perp}}{v}. \tag{5}$$

Starting from Eq. (4) and consistently developing the continuum theory of FN, we by analogy with Ref. [22] took into account the additional term of fourth order in $(\boldsymbol{m}\cdot\boldsymbol{n})$ in the expansion of orientational energy of ferroparticles. Additionally, we have generalized the idea of Ref. [22] for the homeotropic anchoring on the case of arbitrary uniform boundary conditions for the director on the surface of ferroparticles. Also, we have established the influence of surface elastic constant K_{24} of NLC on the energies $\mathcal{F}'_{\parallel}$ and $\mathcal{F}'_{\perp}$ that are used to estimate the coefficients of the expansion (4). As a result, for the modified orientational energy of ferroparticles the following expression was obtained [1]:

$$\begin{aligned} F_{OR,4}(\theta) &= A_2 f(\boldsymbol{m}\cdot\boldsymbol{n})^2 + A_4 f(\boldsymbol{m}\cdot\boldsymbol{n})^4 \\ &= -2\frac{W}{d}P_2 f(\boldsymbol{m}\cdot\boldsymbol{n})^2[1-\zeta(\boldsymbol{m}\cdot\boldsymbol{n})^2], \\ P_2 &= P_2(\cos\alpha), \quad \zeta = -(A_4/A_2) = \zeta(\cos^2\alpha). \end{aligned} \tag{6}$$

We have shown that theoretical estimate of Ref. [3] for the coefficient A_2 in Eq. (3), determined in the approximation $w \ll 1$, is rather good. In addition, we have obtained that for a large value of the surface saddle-splay constant $K_{24} = (1\text{–}2)K$ of the nematic matrix (see, for example, Refs. [25,26]) this estimate can be used up to the values $w \leqslant 1$. To take into account the coefficient A_4 in the modified orientational energy of ferroparticles we introduce the phenomenological parameter ζ in Eq. (6). In general, its value depends on the FN material parameters and the type of anchoring of the director at the particle surfaces. The possible values of ζ belong to the interval $-1 \leqslant \zeta < \zeta_{BS}$, where the restriction on the upper boundary $\zeta_{BS} = 0.5$ is introduced in order to exclude the existence of a bistable or a tilted orientation of ferroparticles with respect to the nematic director in the absence of an external magnetic field [1].

Analyzing the expression (1)–(6) and tracing the relationship between mesoscopic and continuum descriptions of magnetic suspensions, it is easy to see that, compared with the model [3] of soft FNs, due to the additional phenomenological parameter ζ we make a correction to the energy $(\mathcal{F}'_{\parallel} - \mathcal{F}'_{\perp})$ of a single particle at parallel and perpendicular orientation of its long axis with respect to the nematic director. These corrections, as mentioned above, may be associated with end effects, local deformations of the director near individual particles, and the deviation of the particle shape from cylindrical. However, unlike the approach of Refs. [12,13] in our modified theory of soft FNs these corrections are not taken into account by simple renormalization of the coefficient A_2 (or the anchoring energy W), but due to more complete [up to fourth order in $(\boldsymbol{m}\cdot\boldsymbol{n})$] description of ferroparticle orientational energy.

The higher-order contributions (A_6, A_8, and so on) in Eq. (6) for the particle orientational energy are related to more subtle effects such as small differences of particles in sizes, a local heterogeneity of surface relief of particles, a local heterogeneity of boundary conditions on the particles, etc. In our opinion an inclusion of these contributions in Eq. (6) exceeds the accuracy of the FN free energy density

proposed in [1]. Therefore, higher-order contributions were not considered in Ref. [1] for description of FNs.

Below, based on the proposed modified model of soft FNs, we consider the influence of additional contribution of the fourth order in $(\boldsymbol{m}\cdot\boldsymbol{n})$ in the orientational energy of ferroparticles on the behavior of magnetic suspensions in an external magnetic field. The paper is structured as follows.

Section II provides detailed theoretical description of the orientational states of FN: homeotropic (A), angular (B), and parallel (C), which were predicted in Ref. [9]. As a sample we consider unbounded FN and obtain the expression for the free energy density corresponding to the given case. On the basis of this expression, we obtain the equations of equilibrium for the orientational angles of the director $\boldsymbol{n}$ and the magnetization $\boldsymbol{m}$ in an external magnetic field and determine the energies of the orientational states and the critical values of the fields that correspond to the absolute instability of the states A and C. In Sec. III we show that for the unbounded FN the modified form (6) of the orientational energy of soft FNs leads to new results. In particular, to the conclusion that FN transitions between states A, B, and C can be both second-order and first-order transitions, and for certain values of ζ the angular state B can be only metastable. In Sec. IV, we propose the theoretical description of the experiment on the birefringence of FN in a magnetic field. Here we show the possibility of observing the orientational states A, B, and C and describe the features of the transitions of the first and second order between the states. It is established that at the transitions of the first order the orientational hysteresis can be observed, caused by the simultaneous existence of thermodynamically stable and metastable FN states in an external magnetic field. It is also shown that depending on the value of ζ there are five types of hysteresis loops, whose character can be observed in experiments on FN birefringence. The obtained results are generalized in Sec. V.

II. UNBOUNDED FERRONEMATIC IN A MAGNETIC FIELD

A. Free energy and equilibrium equations

Let us consider the influence of the modified form (6) of ferroparticles orientational energy on regions of existence of homeotropic (A), angular (B), and parallel (C) states with various mutual orientation of the director $\boldsymbol{n}$ and magnetization vector $\boldsymbol{m}$ in uniform magnetic field (see Fig. 1), and also let us discuss the character of transitions between these states depending on the phenomenological parameter ζ. Within the model [3] of soft FNs this study was carried out in Ref. [9], where an unbounded sample of FN was considered. Using the unbounded sample for the description of orientation states A, B, and C in comparison with their study in finite volumes of FN gives the following advantages. First, at equilibrium the unbounded FN sample does not contain the director field deformations at scales $r \gg L$; therefore, in the density F of FN free energy (the general expression for which is presented in Ref. [1]) the Frank energy of these deformations is identically zero. Second, the concentration of the particles remains constant in each small bulk of FN, and the so-called segregation effect [2,3] associated with the spatial redistribution of ferroparticles under external magnetic field action is absent. Third, such consideration eliminates an influence of cell walls on the orientational behavior of a magnetic suspension. Therefore, for unbounded FN in the free energy density remains three terms:

$$F = F_{OR,4} + F_{DP} + F_{QP}. \tag{7}$$

The first term in Eq. (7) is modified orientational energy from Eq. (6). The contribution

$$F_{DP} = -M_S f(\boldsymbol{m}\cdot\boldsymbol{H}) \tag{8}$$

describes the dipole mechanism of ferroparticle ensemble interaction with an external magnetic field. The term

$$F_{QP} = -\frac{\chi_a}{2}(\boldsymbol{n}\cdot\boldsymbol{H})^2 \tag{9}$$

corresponds to quadrupole interaction of nematic matrix with the external field and is the diamagnetic energy of NLC, where χ_a is the anisotropy of diamagnetic susceptibility. Therefore, the use of the unbounded ferronematic liquid crystal for study of ferronematic phases A, B, and C, allows us to investigate the direct competition between the orientational interaction of particles with the nematic matrix, dipole, and quadrupole interactions of FN with the external magnetic field.

Now we turn directly to a formulation of the problem. Let us consider the unbounded uniform FN sample with the director $\boldsymbol{n}$ along which we direct the x axis of the Cartesian coordinate; see Fig. 2. We assume that the NLC has positive diamagnetic anisotropy ($\chi_a > 0$), and the homeotropic type of anchoring ($\alpha = \pi/2$) takes place at the surfaces of particles. At this anchoring the coefficient $A_2 = -[2WP_2(0)/d] = (W/d) > 0$; therefore, in the absence of magnetic field the particles are oriented in the planes which are perpendicular to the director. Now we direct the magnetic field $\boldsymbol{H} = (0,H,0)$ along the y axis. For $H \sim 1$Oe it plays the role of the bias field [1,3] and magnetizes the FN to the saturation, orienting the ferroparticle magnetic moments in the direction of $\boldsymbol{H}$ (along the y axis). As the field increases, the director also tends to orient along to the field due to $\chi_a > 0$; see Eq. (9). Thus, there occurs a competition between different mechanisms of orientation ordering of FN.

It is convenient to write the components of the director and magnetization unit vector in the form

$$\boldsymbol{n} = (\cos\phi,\ \sin\phi,\ 0), \tag{10}$$

$$\boldsymbol{m} = (-\sin\psi,\ \cos\psi,\ 0), \tag{11}$$

where the angles ϕ and ψ determine the deviations $\boldsymbol{n}$ and $\boldsymbol{m}$ from the directions of their initial orientation $\phi_0 = \psi_0 = 0$,

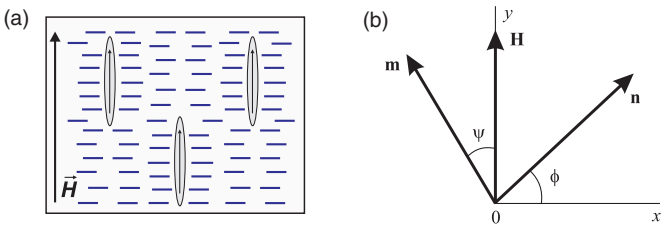

FIG. 2. (Color online) Unbounded FN in the external magnetic field (a); choice of the coordinate system (b).

i.e., $\boldsymbol{n} = (1, 0, 0)$ and $\boldsymbol{m} = (0, 1, 0)$; see Fig. 2(b). Substituting (10) and (11) into (7), we obtain

$$F = \frac{W}{d} f \sin^2(\phi - \psi)[1 - \zeta \sin^2(\phi - \psi)] - M_s f H \cos\psi - \frac{1}{2}\chi_a H^2 \sin^2\phi, \tag{12}$$

where for the parameter $\zeta = \zeta(0)$ corresponding to the homeotropic anchoring ($\alpha = \pi/2$), we left the same notation, as in (6).

It is convenient to write Eq. (12) in dimensionless variables, taking $H_0 = M_s f/\chi_a$ (representing a characteristic field of transition from dipolar to a quadrupolar ordering regime [27]) as a unit of field strength. Thus, $H = H_0 h$, where h is the dimensionless field strength. Let us introduce also the dimensionless orientational energy of magnetic particles $\omega = (W\chi_a/dM_S^2 f)$; as a result we obtain

$$F = \chi_a H_0^2 \left\{\omega \sin^2(\phi - \psi)[1 - \zeta \sin^2(\phi - \psi)] - h\cos\psi - \tfrac{1}{2}h^2 \sin^2\phi\right\}. \tag{13}$$

The equations of FN orientational equilibrium are obtained by minimization of free energy (13) with respect to ϕ and ψ; hence,

$$h^2 \sin\phi\cos\phi - \omega \sin 2(\phi - \psi)[1 - 2\zeta \sin^2(\phi - \psi)] = 0, \tag{14}$$

$$h \sin\psi - \omega \sin 2(\phi - \psi)[1 - 2\zeta \sin^2(\phi - \psi)] = 0. \tag{15}$$

Let us consider the solutions of these equations which correspond to the different orientational states of FN.

B. Orientational states of FN

The set of orientation equilibrium equations (14) and (15) has three solutions satisfying the conditions of free energy minimum

$$\frac{\partial^2 F}{\partial\phi^2} \geqslant 0, \quad \frac{\partial^2 F}{\partial\phi^2}\frac{\partial^2 F}{\partial\psi^2} - \left(\frac{\partial^2 F}{\partial\phi\partial\psi}\right)^2 \geqslant 0. \tag{16}$$

These solutions correspond to uniform ferronematic states; we classify them by analogy with Ref. [9].

(i) The trivial solution $\phi_A = \psi_A = 0$ corresponds to the unperturbed configuration, i.e., $\boldsymbol{n} = (1, 0, 0)$ and $\boldsymbol{m} = (0, 1, 0)$. This state is characterized by the perpendicular orientation of the director with respect to the magnetization unit vector and to the external magnetic field direction: $\boldsymbol{n}\perp\boldsymbol{m}||\boldsymbol{H}$. It is called "*homeotropic FN state*"; see state A in Fig. 1.

(ii) The solution of a general form when ϕ and ψ are different from zero and $(\pi/2)$ corresponds to the so-called [9] "*angular FN state*" or state B in Fig. 1. For this configuration, the angles of director orientation $\phi_B = \phi_B(h,\omega,\zeta)$ and magnetization unit vector $\psi_B = \psi_B(h,\omega,\zeta)$ are determined from the system of Eqs. (14) and (15) and are the functions of magnetic field strength, material parameters of the system and phenomenological parameter ζ.

(iii) The third solution corresponds to the values $\phi_C = \pi/2$ and $\psi_C = 0$, i.e., $\boldsymbol{n} = (0,1,0)$ and $\boldsymbol{m} = (0, 1, 0)$. It describes "*parallel FN state*" or state C in which the director and ferroparticle magnetic moments are oriented along the field $\boldsymbol{n}||\boldsymbol{m}||\boldsymbol{H}$; see Fig. 1.

From equilibrium equations (14) and (15) it is possible to find the critical values of fields, at which the homeotropic (A) and parallel (C) states are absolutely unstable. All we have to do is to linearize Eqs. (14) and (15) near $\{\phi_A = 0, \psi_A = 0\}$ for state A and near $\{\phi_C = \pi/2, \psi_C = 0\}$ for state C. Solutions of the linearized equations show that the homeotropic state is absolutely unstable at $h > h_\perp$, where

$$h_\perp = \sqrt{\omega^2 + 2\omega} - \omega, \tag{17}$$

and the parallel state is absolutely unstable at $h < h_\parallel$, here

$$h_\parallel = \sqrt{\omega^2(1 - 2\zeta)^2 + 2\omega(1 - 2\zeta)} + \omega(1 - 2\zeta). \tag{18}$$

More complete information about existence areas of each orientational state—A, B, and C—can be obtained by comparison of their free energies in the magnetic field h. For these states the dimensionless [divided by $\chi_a H_0^2$; see Eq. (13)] values of free energies per unit volume of FN are as follows:

$$\begin{aligned} F_A &= -h, \\ F_B &= \omega \sin^2(\phi_B - \psi_B)[1 - \zeta \sin^2(\phi_B - \psi_B)] \\ &\quad - h\cos\psi_B - \frac{1}{2}h^2 \sin^2\phi_B, \\ F_C &= \omega(1 - \zeta) - h\left(1 + \frac{h}{2}\right). \end{aligned} \tag{19}$$

The comparative analysis of these energies is given in the following section.

III. ORIENTATIONAL TRANSITIONS IN FERRONEMATICS

A. General description

First of all, we briefly discuss the results of Ref. [9], where the comparison of energies (19) is carried out within the framework of the model [3] of soft FN, i.e., at $\zeta = 0$. In this case the increase of external magnetic field h leads to consecutive orientational transitions from state A to state B at $h = h_\perp$, and then to state C at $h = h_\parallel(\zeta = 0)$. Both transitions between the states are the transitions of the second order when the order parameter (which can be, e.g., $\sin^2\phi$ or $\sin^2\psi$) smoothly varies at the transition point.

In the considered case, i.e., at $\zeta \neq 0$, the situation becomes more complicated. As calculations show, the critical fields of transitions between states and the character (the second or first order) of these transitions depend on the values of ω and ζ. Let us remind the reader that the transition of the first-order is characterized by a jump of order parameter ($\sin^2\phi$ or $\sin^2\psi$) at the transition point.

A general picture of the regions of existence of orientational states A, B, and C in the plane (ω,ζ) at the considered values of ζ from the interval $-1 \leqslant \zeta < \zeta_{BS} = 0.5$, as well as the character of transitions between the states are presented in Fig. 3. Here the plane (ω,ζ) is divided into three regions by curves $\zeta_\perp(\omega)$ and $\zeta_\parallel(\omega)$, which are depicted by solid lines. The physical meaning of these curves is discussed below. Within $-1 \leqslant \zeta < \zeta_\parallel$ all of three orientational states A, B, and C can exist consistently (with the increase of h), and transitions

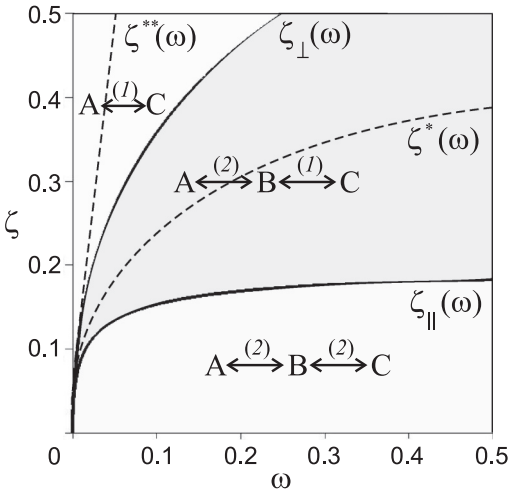

FIG. 3. Regions of existence of orientational states A, B, and C induced by magnetic field in the plane (ω,ζ). Symbols (*1*) and (*2*) show the character of equilibrium transitions between the states (first or second order). The tricritical curves $\zeta_{\parallel}(\omega)$ and $\zeta_{\perp}(\omega)$ are calculated with use of Eqs. (22) and (23). The curves $\zeta^{*}(\omega)$ and $\zeta^{**}(\omega)$ correspond to Eqs. (26) and (28).

between the states in the external magnetic field are transitions of the second order, as well as at $\zeta = 0$ [9]. For $\zeta_{\parallel} < \zeta < \zeta_{\perp}$ the orientational states also consistently exist at the increase of h, but the transition from the angular state B to the parallel state C becomes a transition of the first order. For $\zeta_{\perp} < \zeta < \zeta_{BS}$ only two states are stable—homeotropic (A) and parallel (C)—and the transition between these states in the external field is a transition of the first order. As is obvious from the above, the curves $\zeta_{\perp}(\omega)$ and $\zeta_{\parallel}(\omega)$, i.e., the boundaries of the mentioned regions, play a role of tricritical dependences: They correspond to the points of the plain (ω,ζ) at which the transition character changes from the second-order to the first-order one (and vice versa).

It should be noted that in Fig. 3 we show also the critical curves $\zeta^{*}(\omega)$ and $\zeta^{**}(\omega)$, which correspond to the qualitative change of the orientational hysteresis loop in the magnetic field. At this stage we do not pay special attention to them as the phenomenon of a hysteresis is in detail discussed in Sec. IV. Here we consider equilibrium transitions between the FN orientational states, study the behavior of magnetic suspensions in each of three regions described above, and give relations corresponding to the tricritical dependences $\zeta_{\perp}(\omega)$ and $\zeta_{\parallel}(\omega)$.

B. Second-order transitions at $-1 \leqslant \zeta < \zeta_{\parallel}$

Figure 4 presents the dependencies of free energy density of orientational states A, B, and C on the dimensionless magnetic field h specific for $-1 \leqslant \zeta < \zeta_{\parallel}$, and also the dependences of deviation angles of the director ϕ and the magnetization unit vector ψ corresponding to these states on h at $\omega = 0.1$ and $\zeta = 0.1$. The energy point of reference in Fig. 4(a) is represented by the energy F_A of homeotropic (A) state; therefore, the value of ΔF_A corresponds to the abscissa axis for this state, and the functions $\Delta F_B = F_B - F_A$ and $\Delta F_C = F_C - F_A$ with the energies from Eq. (19) correspond to the angular (B) and

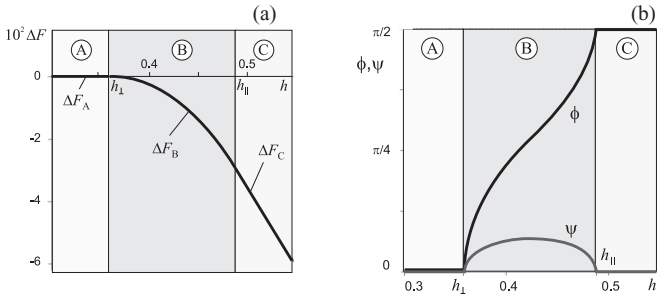

FIG. 4. Regions of existence of orientational states A, B, and C in the magnetic field h for $\omega = 0.1$ and $\zeta = 0.1$: (a) free energy density of the states; (b) deviation angles of the director ϕ and the magnetization unit vector ψ.

parallel (C) states, respectively. The critical fields $h_{\perp} = 0.358$ and $h_{\parallel} = 0.488$ of absolute instability of states A and C shown in this figure are calculated with the use of Eqs. (17) and (18) for $\omega = 0.1$ and $\zeta = 0.1$. Thermodynamically stable sections of curves in Fig. 4 and the subsequent figures are shown by solid lines.

From Fig. 4 it can be seen that in weak magnetic fields which correspond to the values $h < h_{\perp}$, the initial homeotropic state A is stable. In this case, the ordering of FN occurs mostly in a dipole (8) mode of interaction of the magnetic field with the ensemble of ferroparticles, and this interaction makes the main magnetic contribution to free energy density (7) of the system. Because the orientational energy of ferroparticles possesses the minimum at $\boldsymbol{m} \perp \boldsymbol{n}$, in weak fields the director $\boldsymbol{n}$ and magnetization vector $\boldsymbol{m}$ keep their initial orientation: $\boldsymbol{n} = (1, 0, 0)$ and $\boldsymbol{m} = (0, 1, 0)$. The homeotropic state A is stable until the magnetic field strength reaches the threshold value $h_{\perp}$. At $h = h_{\perp}$ it transforms into angular state B. At that, the values of orientation angles of the director ϕ and magnetization ψ vary smoothly at the transition point that corresponds to the transition of the second order [see Fig. 4(b)]. Due to positive diamagnetic anisotropy ($\chi_a > 0$), at $h > h_{\perp}$ the LC director deviates in the direction of a field. In this case the ensemble of ferroparticles is affected by two mechanisms of ordering: dipole (interaction with the external field) and orientational (interaction with the nematic matrix). The competition of these mechanisms results in a deviation of the magnetization unit vector from the direction of its initial orientation. Thus, above the transition point the angles ϕ and ψ possess nonzero values, and their difference $(\phi - \psi) \neq 0$ and $\pi/2$, which is a characteristic feature of the angular state B.

In the angular state B, with the increase of the magnetic field strength the function $\phi_B(h)$ monotonically increases from zero at $h = h_{\perp}$ up to $(\pi/2)$ at $h = h_{\parallel}$. The function $\psi_B(h)$, in its turn, increases from zero at $h = h_{\perp}$, reaches its maximum, and then again becomes zero at $h = h_{\parallel}$. Thus, at $h = h_{\parallel}$ the angular state B transforms into the parallel state C. In the state C the magnetic interactions (dipole and quadrupole) of FN with the external field suppress the orientational interaction of particles with the nematic matrix. Therefore, the director $\boldsymbol{n}$ and magnetization vector $\boldsymbol{m}$ line up along the field direction. From Fig. 4(b) one can see that the angles ϕ and ψ, and therefore the order parameter, vary smoothly at the transition

point; i.e., this transition, as well as the transition at $h = h_\perp$, is the second-order transition. For $-1 \leqslant \zeta < \zeta_\parallel$ the parallel state C remains stable at $h > h_\parallel$.

C. First- and second-order transitions at $\zeta_\parallel < \zeta < \zeta_\perp$

As calculations show, the second-order transition at $h = h_\parallel$ from the angular state B into the parallel state C does not remain the same at any values of ζ. This can be seen by considering the behavior of $\phi_B(h)$ and $\psi_B(h)$ near the transition point. Using in equilibrium Eqs. (14) and (15) the approximations $(\pi/2 - \phi) \ll 1$ and $\psi \ll 1$ for $(h_\parallel - h) \ll h_\parallel$ we obtain the following form of the solutions:

$$\phi_B \approx \frac{\pi}{2} - \sqrt{D(h_\parallel - h)}, \quad \psi_B \approx h_\parallel \sqrt{D(h_\parallel - h)}, \tag{20}$$

$$D = \frac{2(1-2\zeta)(2+h_\parallel)}{h_\parallel[h_\parallel(2+h_\parallel)^2 - 2\zeta(3h_\parallel^3 + 10h_\parallel^2 + 10h_\parallel + 2)]}. \tag{21}$$

As it is seen from Eq. (20), the character of the transition depends on a sign of D. For $D > 0$ the orientational transition of the second order takes place, in this case with the increase of the field strength h up to $h_\parallel$ the angle ϕ_B smoothly increases and ψ_B smoothly decreases [as in Fig. 4]. For $D < 0$ the first-order transition occurs, when the orientations of the director and unit vector of magnetization change discontinuously near $h_\parallel$. At the tricritical point where the transition of the second order changes to the first-order one (and vice versa), the value of D has to tend to infinity. It means that the denominator in Eq. (21) should be zero. As the field $h_\parallel$ from Eq. (18) is the function of the parameters ω and ζ, the obtained equation

$$h_\parallel(2+h_\parallel)^2 - 2\zeta(3h_\parallel^3 + 10h_\parallel^2 + 10h_\parallel + 2) = 0 \tag{22}$$

determines the tricritical dependence which in Fig. 7 is designated as $\zeta_\parallel(\omega)$. For $\zeta < \zeta_\parallel$ the transition from the angular state B to the parallel state C is the transition of the second order, and for $\zeta > \zeta_\parallel$ this is the transition of the first order.

The dependencies $\Delta F(h)$, $\phi(h)$, and $\psi(h)$ for orientational states A, B, and C, typical for $\zeta_\parallel < \zeta < \zeta_\perp$, are shown in Fig. 5 at $\omega = 0.1$ and $\zeta = 0.25$. For the given parameters ω and ζ the critical field $h_\parallel$ corresponds to 0.370, and the tricritical point $\zeta_\parallel = 0.153$.

From Fig. 5 it can be seen that in weak fields, i.e., at $h < h_\perp$, the homeotropic state A is stable. At $h = h_\perp$ the second-order transition into angular state B takes place. In this state, as the external magnetic field increases, the functions $\phi_B(h)$ and $\psi_B(h)$ monotonically increase from zero at $h = h_\perp$ to the certain values ϕ_P and ψ_P at $h = h_P$, when the orientational transition to the parallel state C occurs with the angles $\phi_C = \pi/2$ and $\psi_C = 0$. Thus, the order parameter for this transition changes discontinuously; i.e., this transition is of the first order. The threshold field h_P and the corresponding critical values of ϕ_P and ψ_P are functions of the material parameters and phenomenological parameter ζ. They can be found from Eqs. (14) and (15) and the condition of equality of free energies of parallel and angular FN states, i.e., $F_B = F_C$. For the case shown in Fig. 5, the field of the first-order transition and critical angles correspond to the values $h_P = 0.395$, $\phi_P = 0.776 = 0.247\pi$, and $\psi_P = 0.199 = 0.063\pi$.

Metastable segments of dependences $\phi(h)$ and $\psi(h)$ for the angular and parallel states are shown in Fig. 5(b) by the dashed lines. As it is seen, the state C is metastable within $h_\parallel \leqslant h < h_P$, and at $h > h_P$ this state becomes thermodynamically stable.

D. First-order transition at $\zeta_\perp < \zeta < \zeta_{BS}$

As ζ increases, the critical value of the field h_P of the first-order transition between the angular B and parallel C states shifts towards smaller values of h. At the certain $\zeta = \zeta_\perp$ this value becomes equal to the field $h_\perp$ of the second-order transition from the homeotropic A state to the angular B one. From Fig. 5 it is seen that in this case, the angular state becomes metastable, and the second-order transition from state A into state B becomes the first-order transition from state A into state C. Therefore, at $h_P = h_\perp$ the energies of all three states have to be equal to each other. For the homeotropic and parallel states this is equivalent to $F_A = F_C$ at $h = h_\perp$, which allows us to determine the tricritical dependency $\zeta_\perp(\omega)$, shown in Fig. 3; it is obtained from the following expression [coincidence of expressions (23) for $\zeta_\perp(\omega)$ and (17) for $h_\perp$ is formal]

$$\zeta_\perp(\omega) = \sqrt{\omega^2 + 2\omega} - \omega. \tag{23}$$

The characteristic behavior of FN in the external magnetic field for $\zeta_\perp < \zeta < \zeta_{BS}$ is clearly illustrated in Fig. 6; here the tricritical point $\zeta_\perp$ at $\omega = 0.1$ corresponds to 0.358, and the absolute instability boundary of the parallel state at $\omega = 0.1$

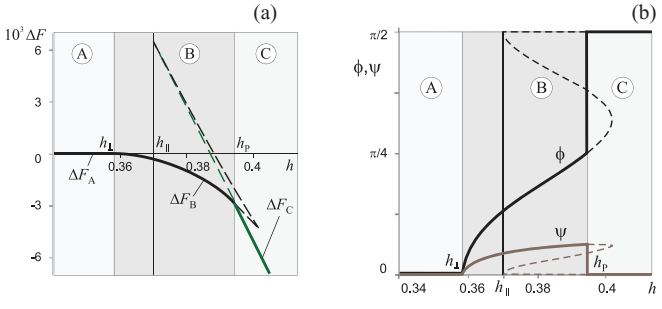

FIG. 5. (Color online) Regions of existence of orientational states A, B, and C in the magnetic field h for $\omega = 0.1$ and $\zeta = 0.25$: (a) free energy density of the states; (b) deviation angles of the director ϕ and the magnetization unit vector ψ.

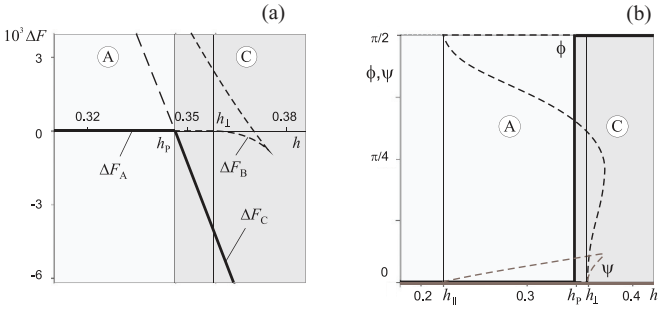

FIG. 6. (Color online) Regions of existence of orientational states A and C in the magnetic field h for $\omega = 0.1$ and $\zeta = 0.4$: (a) free energy density of the states; (b) deviation angles of the director ϕ and the magnetization unit vector ψ. In this case the state B can be only metastable.

and $\zeta = 0.4$ corresponds to the critical field $h_{\parallel} = 0.221$. From the presented dependencies it can be seen that in the external field at $\zeta_{\perp} < \zeta < \zeta_{BS}$ the angular state can be only metastable, and the other two states—homeotropic A and parallel C—are thermodynamically stable. The critical value of the field h_P of the first-order transition between these states can be found from the condition $F_A = F_C$, that for $\omega = 0.1$ and $\zeta = 0.4$ results in $h_P = 0.346$. The homeotropic state is stable at $h < h_P$ and metastable for $h_P < h \leqslant h_{\perp}$. The parallel state is metastable at $h_{\parallel} < h < h_P$ and becomes thermodynamically stable at $h > h_P$.

IV. ORIENTATIONAL HYSTERESIS AND BIREFRINGENCE OF A FN

A. Optical properties of a FN in the magnetic field

The orientational transitions between the FN states with various mutual orientation of the director $\boldsymbol{n}$ and magnetization unit vector $\boldsymbol{m}$ studied above can be observed experimentally when a light beam passes through the ferronematic. Let us go back to the geometry in Fig. 2 and assume that the light is incident along the vector $\boldsymbol{H}$, i.e., perpendicular to the director (optical axis) of the initial homeotropic (A) state. The magnetic field induces the rotation of the director and at the critical field values shown above, it initiates the equilibrium transitions to the angular (B) and parallel (C) states (or directly to the parallel state C). In this case the birefringence $\Delta n = n_{\text{eff}} - n_o$ of the liquid crystal matrix of a FN changes; here n_{eff} is the effective refraction index which is defined by

$$\frac{1}{n_{\text{eff}}^2} = \frac{\sin^2\phi}{n_o^2} + \frac{\cos^2\phi}{n_e^2}, \tag{24}$$

where n_o and n_e are the refraction indices of ordinary and extraordinary rays, respectively.

In the homeotropic state $\phi = 0$ and from Eq. (24) it follows that $n_{\text{eff}} = n_e$; i.e., the birefringence $\Delta n = n_e - n_o$ is maximal. In the parallel state, $\phi = \pi/2$, $n_{\text{eff}} = n_o$, and $\Delta n \equiv 0$. The intermediate values of birefringence $0 < \Delta n < n_e - n_o$ correspond to the angular state when $0 < \phi < \pi/2$. If we introduce the parameter $\xi = (n_e^2 - n_o^2)/n_e^2$, then it is convenient to take the reduced value of birefringence as the FN optical characteristic,

$$\frac{\Delta n}{n_o} = \frac{1}{\sqrt{1 - \xi\cos^2\phi}} - 1. \tag{25}$$

Let us discuss the character of the FN birefringence expected in experiments, and demonstrate how the transitions of the first and second order between the orientational states A, B, and C can exhibit themselves. For that, let us go to Fig. 7 showing the dependence $[\Delta n(h)/n_0]$ at $\omega = 0.1$ and $\zeta = 0.25$ as an example. For calculation of this dependence for the nematic matrix of FN the following parameters of liquid crystal 5CB were used: $n_o = 1.53$ and $n_e = 1.71$ for the light wavelength $\lambda_{\text{light}} = 632.8$ nm [28]. In this case $\xi = 0.2$.

The results obtained in Sec. III C show that the transitions of both the first and the second order occur in the ferronematic liquid with the parameters $\omega = 0.1$ and $\zeta = 0.25$ under the action of the external magnetic field. From Fig. 7 it is seen that the second-order phase transition from state A to state B

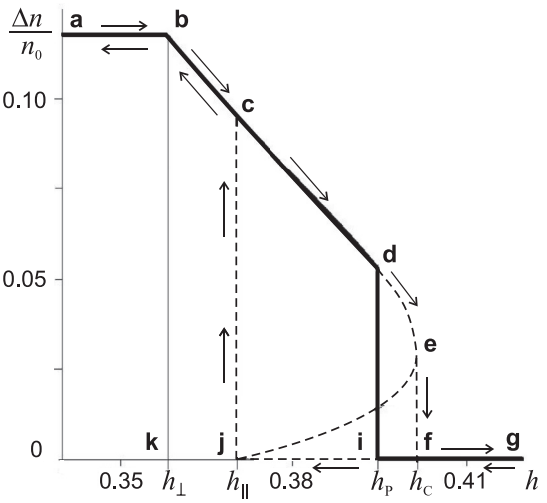

FIG. 7. The reduced value of birefringence $(\Delta n/n_0)$ as a function of the magnetic field h for $\omega = 0.1$ and $\zeta = 0.25$. Arrows show plots of $[\Delta n(h)/n_0]$, which can be observed in the experiment at the increasing and decreasing of magnetic field.

can be detected through the smooth change of birefringence at $h = h_{\perp}$. At the same time the first-order transition from state B to state C is accompanied by the stepwise change of birefringence near $h = h_P$. This transition, as well as first-order transitions in other systems, can be accompanied by the hysteresis phenomena. It is connected with the existence of metastable states of FN near $h = h_P$: the angular state B at $h_{\parallel} \leqslant h \leqslant h_C$ and the parallel state C at $h_{\parallel} \leqslant h < h_P$. Thus, the greatest possible hysteresis loop designated in Fig. 7 by the letters {cdefijc}, is bounded from below by $h = h_{\parallel}$, and from above by $h = h_C$. Let us remind the reader that the field $h_{\parallel}$ is the point of absolute instability of parallel state C and is determined by Eq. (18). The value h_C is introduced here for the first time; it corresponds to the maximal field strength of existence of the solution of Eqs. (14) and (15) for the angular state B. In the considered case, i.e., at $\omega = 0.1$ and $\zeta = 0.25$, the field h_C is equal to 0.402 and as it was already mentioned above, at that value the angular state is metastable ($h_C > h_P$). Now let us show in more detail how the reduced birefringence $(\Delta n/n_0)$ changes first at the increase of the dimensionless strength h of external magnetic field and then at its decrease.

When h increases up to the value $h = h_{\perp}$ then the homeotropic state A is thermodynamically stable and the FN birefringence is maximal; see plot {ab} in Fig. 7. The second-order transition to the angular state B occurs when $h = h_{\perp}$, i.e., at the point {b}, and as h increases, the birefringence decreases smoothly. At first, the dependence $[\Delta n(h)/n_0]$ goes along the thermodynamically stable section of the curve {bcd}, and then, passing at $h = h_P$ the certain point {d} of the first-order equilibrium transition into the parallel state C, it can come to the metastable section {de} of existence of the angular state. At such change of birefringence, the observed transition of the first-order to state C in the increasing external magnetic field corresponds to the value $h = h_C$, i.e., the point {e} of $[\Delta n(h)/n_0]$. At the point {e} the birefringence jumps to zero; see plot {ef}. With a further increase of the field, the FN

birefringence remains equal to zero [see plot {fg}], since at $h > h_C$ the parallel state C is thermodynamically stable.

When h decreases from the values exceeding the critical field h_C, the curve $[\Delta n(h)/n_0]$ first goes along the thermodynamically stable section {gfi}, which corresponds to the parallel state C and zero value of birefringence. Then, passing at $h = h_P$ the certain point {i} of the first-order equilibrium transition into the angular state B, the ferronematic can keep the parallel orientation of $\boldsymbol{n}$ and $\boldsymbol{m}$, being thus in the metastable state [see plot {ij} in Fig. 7]. The lower boundary of existence of the parallel metastable state C and the lower boundary of the first-order transition between states C and B (which can be experimentally observed at the decreasing of h), is the field $h = h_\parallel$, i.e., the point {j} of the curve $[\Delta n(h)/n_0]$. At the point {j} the reduced birefringence of FN jumps from zero to the finite value $[\Delta n(h = h_\parallel)/n_0]$, corresponding to the angular state [see plot {jc}]. With the further field decrease the birefringence smoothly increases at the angular state [see plot {cb}]. At the point {b}, i.e., at $h = h_\perp$, the second-order transition to the homeotropic state A occurs, and the birefringence reaches its maximum.

B. Shape of hysteresis loop

Now let us discuss how from a qualitative viewpoint a hysteresis loop shape varies depending on the parameters ω and ζ. Let us define a width of hysteresis loop $\Delta h = h_C - h_\parallel$. It is obvious that Δh depends on ω and ζ, since at different relations between them, h_C and $h_\parallel$ can change as well as the character of the transitions between the FN orientational states. Thus, a shape of hysteresis loop can change qualitatively, and this undoubtedly will be observed in experiments.

In Sec. III we showed that in the plane (ω,ζ) there are three regions where the equilibrium transitions between the FN orientational states have different characters; see Fig. 3. Looking ahead, we can say that the variations of hysteresis loop have broader gradation: At the plane (ω,ζ) there are five regions where the hysteresis loop contains qualitatively different plots which correspond to thermodynamically stable or metastable states of FN. These five regions at the plane (ω,ζ), for which the hysteresis loop can differently behave in the experiments, are divided by the curves $\zeta_\parallel(\omega)$, $\zeta^*(\omega)$, $\zeta_\perp(\omega)$, and $\zeta^{**}(\omega)$; see Fig. 3. The shape of hysteresis loop for each of these regions is schematically shown in Fig. 8. Let us discuss qualitative differences between the hysteresis loops of various regions, estimate their width Δh, and obtain general expressions for the dependences $\zeta^*(\omega)$ and $\zeta^{**}(\omega)$.

As is shown below, qualitative differences in the orientational behavior of FN which can be observed in experiments on birefringence are connected with various relations between the critical fields $h_\perp$, $h_\parallel$, h_P, and h_C. Their values depend on ω and ζ so that each of five regions of the plane (ω,ζ) shown in Fig. 3 corresponds to a certain relation between the critical fields.

Let us consider the region $-1 \leqslant \zeta < \zeta_\parallel$. As shown above, here the condition $h_\perp < h_\parallel = h_P = h_C$ is satisfied, and equilibrium transitions from state A to state B and then to state C are the second-order transitions, and the hysteresis loop width $\Delta h = h_C - h_\parallel \equiv 0$. Therefore, in the range of values of ω and ζ the hysteresis should not be observed in experiments; see Fig. 8(a).

For $\zeta_\parallel < \zeta < \zeta^*$ the dependence of birefringence on the external magnetic field strength is shown in Figs. 7 and 8(b). Here $h_\perp < h_\parallel < h_P < h_C$, and the width of hysteresis loop $\Delta h = h_C - h_\parallel$, the equilibrium transition from state A to state B is the second-order transition, and the transition between states B and C is the first-order transition. The type of hysteresis loop for this region is in detail described in Sec. IV A. In particular, it is shown that all three states—homeotropic, angular, and parallel—should be observed in the experiment, both at increase and at decrease of external magnetic field. However, such behavior of the system does not remain the same at any values $\zeta > \zeta_\parallel$: At a given ω, the increase of parameter ζ results in decreasing of the critical fields $h_\parallel$, h_P, and h_C. At that, $h_\perp$ remains constant; see Eq. (17). From Fig. 7 it is easy to understand that at the increase of ζ and decrease of $h_\parallel$, h_P, and h_C the field $h_\parallel$ is the first to reach the value $h_\perp$ at the certain critical value $\zeta = \zeta^*(\omega)$. In this case the plot {jc}, shown in Fig. 7, coincides with the segment {kb}. The further increase of ζ, i.e., decrease of $h_\parallel$, results in the qualitative change of hysteresis loop (see below). Thus, the critical dependence $\zeta^*(\omega)$, which corresponds to that change, can be found from the condition $h_\perp = h_\parallel$; hence,

$$\zeta^* = \frac{\sqrt{\omega^2 + 2\omega} - \omega}{\sqrt{\omega^2 + 2\omega} - \omega + 1}. \tag{26}$$

Let us turn to the case $\zeta^* < \zeta < \zeta_\perp$, corresponding to Fig. 8(c). As compared with the previous case, here the character of equilibrium transitions between states A, B, and C does not change and the loop width remains the same, i.e., $\Delta h = h_C - h_\parallel$. However, the lower boundary $h_\parallel$ of the hysteresis loop changes relative to the field $h_\perp$ of the transition between states A and B since for the critical fields the

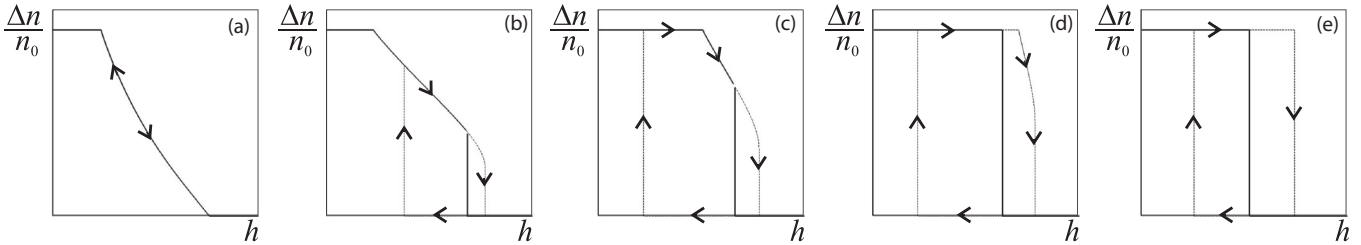

FIG. 8. Qualitative type of hysteresis loop at the birefringence for the regions of the plane (ω,ζ), shown in Fig. 3: $-1 \leqslant \zeta < \zeta_\parallel$ (a), $\zeta_\parallel < \zeta < \zeta^*$ (b), $\zeta^* < \zeta < \zeta_\perp$ (c), $\zeta_\perp < \zeta < \zeta^{**}$ (d), $\zeta^{**} < \zeta < \zeta_{BS}$ (e).

condition $h_\parallel < h_\perp < h_P < h_C$ is satisfied. It means that with the decreasing of magnetic field h the angular state may not be observed in the experiments. Indeed, at $h = h_\parallel$ parallel C state immediately goes into a homeotropic state C, and the birefringence $(\Delta n/n_0)$ jumps from zero to the maximum value $(n_e - n_0)/n_0$. The increase of the parameter ζ in the considered case leads to the further decrease of the critical fields $h_\parallel$, h_P, and h_C at constant $h_\perp$. The relation between the fields $h_\parallel < h_\perp < h_P < h_C$, typical for this case, is broken when the critical field h_P of the first-order equilibrium transition between states B and C reaches the value $h_\perp$. The value $\zeta_\perp$ which corresponds to this condition is determined by Eq. (23).

For $\zeta_\perp < \zeta < \zeta^{**}$ the critical fields satisfy the condition $h_\parallel < h_P < h_\perp < h_C$; the hysteresis loop width presented in Fig. 8(d) is still $\Delta h = h_C - h_\parallel$. As shown above, there are only two states that are stable in this case: homeotropic A and parallel C. Meanwhile, the metastable angular state can be observed in the experiments on birefringence under the increasing magnetic field. This can be seen in the top right segment of the hysteresis loop which corresponds to the metastable angular state B. This segment disappears when at the increase of ζ the field h_C becomes equal to $h_\perp$. The condition $h_C = h_\perp$ takes place at the certain value $\zeta = \zeta^{**}(\omega)$. The dependence $\zeta^{**}(\omega)$ can be found from Eqs. (14) and (15) near $h = h_\perp$, when the orientational distortions are small $\phi \ll 1$ and $\psi \ll 1$. In the lowest order of expansion for the angular phase we have

$$\phi_B \approx \sqrt{E(h - h_\perp)}, \quad \psi_B \approx h_\perp \sqrt{E(h - h_\perp)}, \qquad E = \frac{2(h_\perp + \omega)}{\omega[h_\perp(h_\perp - 2)^2 - 4\zeta(1 - h_\perp)^3]}. \tag{27}$$

At $h_C = h_\perp$ the coefficient E has to go to infinity, i.e., the denominator for E in Eq. (27) should be zero. From this condition one can find the critical dependence $\zeta^{**}(\omega)$, which determines the upper boundary of considered region in the value of ζ:

$$\zeta^{**} = \frac{h_\perp(h_\perp - 2)^2}{4(1 - h_\perp)^3}. \tag{28}$$

Finishing the discussion of FN birefringence, we investigate the shape of hysteresis loop for $\zeta^{**} < \zeta < \zeta_{BS}$; see Fig. 8(e). Here the critical fields satisfy the condition $h_\parallel < h_P < h_\perp = h_C$, the hysteresis loop width is equal to $\Delta h = h_\perp - h_\parallel$, and the shape of the loop becomes rectangular. Only two states—homeotropic and parallel—can be observed at both the increase and the decrease of external field. Thus, at $\zeta^{**} < \zeta < \zeta_{BS}$ the angular state cannot be observed in experiments on birefringence of FN.

V. CONCLUSIONS

In this work in the framework of the modified model of soft FNs proposed in Ref. [1], we have studied the conditions of existence of the homeotropic (A), angular (B), and parallel (C) ferronematic states with different mutual orientations of $\boldsymbol{m}$ and $\boldsymbol{n}$ in an external magnetic field; see Fig. 1. The sample of magnetic suspension considered in this paper represents the unbounded ferronematic liquid crystal with homeotropic anchoring of the director at the particles. In such a system the ferroparticles are aligned perpendicular to the director; therefore, in the absence of a magnetic field for the directions $\boldsymbol{\mu}_i$ of their magnetic moments there is the anisotropy of the "easy plane" type; i.e., the FN initial magnetization $\boldsymbol{M} = M_S f \sum_i \boldsymbol{\mu}_i$ is equal to zero (it is the so-called compensated state of FN [2,3,29]). The weak magnetic field $H \leqslant 1$Oe magnetizes [1,3] the suspension to the saturation in the direction of vector $\boldsymbol{H}$ without any effect on the NLC matrix orientational alignment; so $M = M_S f$. This state corresponds to the homeotropic state A with $\boldsymbol{n} \perp \boldsymbol{m} || \boldsymbol{H}$. At the increase of a magnetic field which strength is characterized by the dimensionless value $h = (H/H_0) = (H\chi_a/M_s f)$, there occurs a competition between the orientational interaction of the particles with the LC matrix, dipole interaction of ferroparticles, and quadrupole interaction of a nematic liquid crystal with the external magnetic field. The result is the orientational transitions to the angular state B, which is characterized by the other than zero and $(\pi/2)$ angle between the vectors $\boldsymbol{m}$ and $\boldsymbol{n}$, and to the parallel state C where $\boldsymbol{n} || \boldsymbol{m} || \boldsymbol{H}$. It is established that the regions of existence of orientational states A, B, and C, and the order (first- or second-) of transitions between states in the external magnetic field depend on the relation between the phenomenological parameter ζ and dimensionless energy $\omega = (W\chi_a/dM_S^2 f)$ of anchoring between particles and the NLC matrix. It is shown also that for the first-order transitions which are characterized by the order parameter jump, the orientational hysteresis occurs in the ferronematic liquid crystal, which depending on ζ and ω may differently behave in the experiments on birefringence of magnetic suspensions. We have determined the regions of the plane (ω,ζ) between which there are the distinctions of this kind (see Fig. 3) and established that in these regions the following behavior is typical for FNs.

(i) At $-1 \leqslant \zeta < \zeta_\parallel$ with the increase of magnetic field strength h there are the consecutive equilibrium transitions of the second order from state A to state B at $h = h_\perp$, and then to state C at $h = h_\parallel$; here the values of $\zeta_\parallel = \zeta_\parallel(\omega)$, $h_\perp = h_\perp(\omega)$, and $h_\parallel = h_\parallel(\omega,\zeta)$ can be found from Eqs. (22), (17), and (18), respectively. The hysteresis loop at $-1 \leqslant \zeta < \zeta_\parallel$ does not occur; see Fig. 8(a).

(ii) At $\zeta_\parallel < \zeta < \zeta_\perp$, first, with the increase of h there occurs the second-order equilibrium transition from state A to state B at $h = h_\perp$, and then at the further increase of the field there occurs the first-order equilibrium transition from state B to state C at $h = h_P$; here the value of $\zeta_\perp = \zeta_\perp(\omega)$ is determined by Eq. (23), and h_P can be found from the equality condition of the energies of angular and parallel states: $F_B = F_C$; see Eq. (19). According to the shape of hysteresis loop this region of ζ values is divided by the curve $\zeta^* = \zeta^*(\omega)$ from Eq. (26) into two parts. Differences in the behavior of FN under the increase and decrease of the magnetic field strength h affecting the shape of the hysteresis loop are explained by the existence of metastable states B and C near the point of the first-order equilibrium transition, i.e., near $h = h_P$. These differences are manifested in the following way:

(a) when $\zeta_\parallel < \zeta < \zeta^*$, all three states (A, B, and C) can be observed in experiments on birefringence of FNs in the magnetic field both increasing and decreasing in h [see Fig. 8(b)];

(b) when $\zeta^* < \zeta < \zeta_\perp$, the states A, B, and C can be observed consecutively only in the increasing field; when h decreases, the plot of the metastable parallel state overlaps the plot of the existence of the angular state, therefore possibly that the latter one cannot be observed in the experiments [see Fig. 8(c)].

(iii) For $\zeta_\perp < \zeta < \zeta_{BS} = 0.5$, the angular state B can be only metastable. States A and C are stable with the first-order equilibrium transition between them in the magnetic field $h = h_P$, here h_P is determined from the condition of equality of energies of homeotropic and parallel states: $F_A = F_C$. For these values of ζ there are also two areas with different characters of the hysteresis loop. These areas are divided by the curve $\zeta^{**} = \zeta^{**}(\omega)$ from Eq. (28), and the behavior of FN at the birefringence has following features:

(a) When $\zeta_\perp < \zeta < \zeta^{**}$, in the increasing field h the metastable angular state B possibly can be observed along with stable states A and C. In the decreasing magnetic field h only states A and C can be observed; see Fig. 8(d).

(b) When $\zeta^{**} < \zeta < \zeta_{BS}$, the angular state cannot be observed in the experiments on the FN birefringence. Only two of the states—A and C—can be observed in both the increasing and the decreasing field; see Fig. 8(e).

Let us note that at $\zeta = 0$ the obtained results coincide with the results of Ref. [9], where the orientational states of FN were investigated in the framework of soft FN model [3]. The latter predicts [9] that in the unbounded FN only transitions of the second order take place between states A, B, and C under the action of the external magnetic field. Our modified theory of soft FNs gives a better understanding concerning the behavior of magnetic suspensions in the external field. First, the present study demonstrates that depending on ω and ζ the transitions between states can be of both the second and the first order. At that, the curves $\zeta_\parallel(\omega)$ and $\zeta_\perp(\omega)$ presented in Fig. 3, play a role of tricritical dependences: They correspond to the values ω and ζ at which the order of the transitions changes from the second to the first one (and vice versa). Second, the obtained results allow us to compare the orientational states of the system and the transitions between states with the FN optical properties. In particular, the second-order transitions in the experiments can be detected due to the smooth change of the magnetic suspension birefringence Δn [see Eq. (25)], and the first-order transitions can be detected due to the stepwise behavior of Δn. By the shape of the hysteresis loops it is possible to estimate ω and ζ for real FNs, and further it will help us to predict the behavior of magnetic suspensions and changes of their optical properties in different devices. It is very important from the viewpoint of possible applications.

Being focused on real thermotropic suspensions, let us give the estimates for the dimensionless parameter ω and characteristic fields

$$H_\perp = h_\perp H_0 = \frac{W}{M_s d}\left[\sqrt{1+\frac{2fM_s^2 d}{W\chi_a}} - 1\right],$$
$$H_\parallel = h_\parallel H_0 = \frac{W}{M_s d}\left[(1-2\zeta) + \sqrt{(1-2\zeta)^2 + \frac{2fM_s^2 d}{W\chi_a}(1-2\zeta)}\right], \quad (29)$$

which correspond to the second-order transitions and have the order of magnitude of the first-order transitions fields ($H_P = h_P H_0 \sim H_\perp \sim H_\parallel$). Following Refs. [3,4,17] and assuming $\chi_a \sim 10^{-7}$, $d \approx 7 \times 10^{-6}$ cm, $M_S \approx 5 \times 10^2$ G, $W \sim 5 \times 10^{-2}$ erg/cm^2, and $f \sim 10^{-7}$–10^{-6}, we obtain $\omega \approx 3 \times 10^{-2}$. In this case the fields $H_\perp$ and $H_\parallel$ are about 100 Oe, and their difference $|H_\parallel - H_\perp|$, which characterizes the interval between the orientational transitions, can possess values from one to dozens of oersteds depending on the value of the phenomenological parameter ζ. Thus, the optical effects connected with the existence of various ferronematic states and transitions between them have to be observed in rather weak magnetic fields.

This conclusion is valid not only for FNs with homeotropic anchoring of the director at the particles. The presented results are also true for FNs with the circular boundary conditions for the director at the ferroparticle surface, and at the dimensionless parameter renormalization $\omega \to -2\omega P_2(\cos\alpha)$ according to the law of transformation of A_2 from Eq. (3), for any magnetic suspensions in which particles in the absence of a field are oriented perpendicular to the nematic matrix director. As shown in Refs. [1,3,30], for such suspensions the boundary angle α between the long axis of an individual particle and the direction of easy orientation of the director at its surface lies within the interval $\alpha_* < \alpha \leqslant \pi/2$, where $\alpha_* = \arccos(1/\sqrt{3})$. It should be noted that the similar consideration of ferronematic states can be also performed for other type of magnetic suspensions in which ferroparticle is oriented along the director in the absence of external magnetic fields. This initial orientation of particles is realized at $0 \leqslant \alpha < \alpha_*$ and, in particular, at the longitudinal anchoring at the ferroparticle surfaces, when $\alpha = 0$. At $0 \leqslant \alpha < \alpha_*$ the existence of all three states A, B, and C in the external field is possible in FNs with negative diamagnetic anisotropy of the nematic matrix ($\chi_a < 0$). In this case the parallel state C is initial, and when the field reaches its critical value, the transition to the angular state B and then to the homeotropic state A (or directly to state A) can take place. The qualitative character of those transitions (of the second and/or first order) does not change.

In summary, we note that the magnetic suspensions synthesized by now greatly vary both in nematic solvent, and in dimensions and types of particles of a rigid phase; see, for example, Refs. [4–6,18–21]. Practically in all the experiments the change of FN birefringence in the magnetic field was studied, and in the cells which geometry was close to the considered case, the threshold effects were observed. However, the purposeful study of hysteresis phenomena in the experiments has not been performed. We hope that theoretical results of this paper can give impetus to performing such research.

ACKNOWLEDGMENTS

We thank Professor Yu. L. Raikher and Dr. V. I. Stepanov for useful discussions, and Dr. A. S. Voroshilov for assistance in preparing the figures. A.Z. gratefully acknowledges financial support from the Russian Foundation for Basic Research (Project No. 13-02-96001).

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