Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Macroscopic Properties of Ferronematics Caused by Orientational Interactions on the Particle Surfaces. I. Extended Continuum Model

S. V. Burylov [a b] & Y. L. Raikher [a b]

[a] Transmag Research Institute, Ukrainian Academy of Sciences, Dnepropetrovsk, 320005, Ukraine

[b] Institute of Continuous Media Mechanics, Urals Branch of the Russian Academy of Sciences, Perm, 614061, Russia

Version of record first published: 23 Sep 2006.

To cite this article: S. V. Burylov & Y. L. Raikher (1995): Macroscopic Properties of Ferronematics Caused by Orientational Interactions on the Particle Surfaces. I. Extended Continuum Model, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 258:1, 107-122

To link to this article: http://dx.doi.org/10.1080/10587259508034552

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 107–122
Reprints available directly from the publisher
Photocopying permitted by license only

Macroscopic Properties of Ferronematics Caused by Orientational Interactions on the Particle Sufaces. I. Extended Continuum Model

S. V. BURYLOV and Y. L. RAIKHER

Transmag Research Institute, Ukrainian Academy of Sciences, Dnepropetrovsk, 320005, Ukraine, Institute of Continuous Media Mechanics, Urals Branch of the Russian Academy of Sciences, Perm, 614061, Russia

(Received November 8, 1993; in final form April 20, 1994)

The Brochard-de Gennes continuum model of ferronematics—magnetic suspensions with the nematic liquid-crystalline carrier—is modified to take into account the finiteness of energy of the nematic molecules anchoring on the particle surface. The developed approach is specified to be capable to describe the equilibrium properties of real thermotropic ferronematics.

PACS numbers: 61.30.Gd 75.50.Mm 82.70.Kj

1 INTRODUCTION

Ferronematics (FN) is the name for suspensions of monodomain ferro- or ferrimagnetic particles in nematic liquid crystals (NLC). The most essential feature of these systems is a strong orientational coupling between the disperse phase (ferroparticles) and the liquid-crystalline matrix. The presence of the ferromagnetic admixture enhances the magnetic susceptibility of FN, in comparison with pure NLC, by several orders of magnitude. The applied magnetic field $\boldsymbol{H}$, changing the orientation of the particles, via them affects the texture of the NLC matrix. Therefore it enables to get hold of a full-scale control over the orientational state of FN with the aid of rather weak—much less than 100 Oe—fields.

A continuum theory for FN had been developed[1] prior to the first experimental realizations of these systems.[2–4] The authors of Ref. [1] had proposed and considered magnetic NLC suspensions, whose solid phase consists of needle- or rod-like ferrite particles with the length $L \gg a$ (where a is the NLC molecule size) and diameter $d \simeq L/10$. Such a distinctive anisometricity imparts to the particles a substantial magnetic rigidity thus making small permanent magnets of them. The volume fraction f of particles in FN is supposed to be sufficiently small ($f < 10^{-4}$) in order to be able to ignore the interparticle magnetic dipole–dipole interaction. In Ref. [1] there was derived a set of equations of orientational-elastic equilibrium in FN capable to describe large-scale structures of the director field as well as stationary distributions of concentration, magnetization, etc.

In a composite medium, which FN actually is, each component—the ferroparticle assembly and the NLC matrix—possesses its own set of the orientational degrees of freedom. So, the form of the equilibrium equations essentially depends upon the origin of coupling between the order parameters of the subsystems. In a magnetized FN, where the parallelicity of the particle axes means, simultaneously, the alignment of their magnetic moments, it is reasonable to characterize the state of the orientational order by two intrinsic variables—director $\boldsymbol{n}(\boldsymbol{r})$ and local magnetization $\boldsymbol{M}(\boldsymbol{r})$—both averaged over a spatial scale large in comparison with the particle size L. Therefore, the macroscopic theory of FN should contain at least one parameter responsible for the local correlation between $\boldsymbol{n}$ and $\boldsymbol{M}$. From this point of view the approach proposed in Ref. [1] looks oversimplified, since it takes into account only the asymptotic case of infinitely strong orientational coupling providing, instead of a balanced correlation, an invariable parallelicity of $\boldsymbol{n}$ and $\boldsymbol{M}$.

A serious necessity to generalize the initial form[1] of the continuum model of FN had appeared some ten years later, when the first thermotropic FN were synthesized.[4] Even qualitative observations of response of the latter to the applied magnetic field have shown that the assumption of $\boldsymbol{n}$ and $\boldsymbol{M}$ co-alignment is not valid there. In attempt to explain this fact and work out a theory more adequate to the real situation, we had had to reconsider the surface interactions between NLC and the suspended particle and assess its effect on the orientational coupling of the order parameters $\boldsymbol{n}$ and $\boldsymbol{M}$. In Refs. [5, 6] we have demonstrated that the rigid anchoring approximation ($\boldsymbol{n} \parallel \boldsymbol{M}$) might be used in FN only if the condition

$$Wd/K \gg 1, \tag{1}$$

holds. Here W is the surface density of the anchoring energy of the nematic, and K is the reference value of the NLC orientational-elastic modulus. For the existing MBBA-based FN with the homeotropic surface alignment one should take $W \sim 10^{-3} - 10^{-2}$ dyn/cm and $K \approx 5 \cdot 10^{-7}$ (see [7], for example). Substituting this into Equation (1) together with the given in Refs. [4, 8, 9, 10] value of the transverse diameter of the particles $d \approx 7 \cdot 10^{-6}$ cm, one gets $Wd/K = 10^{-2} - 10^{-1}$ that is apparently not greater than unity. In view of Equation (1), the latter estimate proves explicitly that the rigid anchoring approximation is invalid for thermotropic FN. Hereby we present a continuum model taking into account the finiteness of the surface energy, i.e., valid for the case $Wd/K \leq 1$.

2 ORIENTATIONAL DISTORTIONS CAUSED BY AN ANISOMETRIC PARTICLE EMBEDDED IN A UNIFORM NEMATIC

Let us begin with some single-particle problems which are of fundamental significance for the build-up of the continuum theory. As the first step, it is necessary to determine the character of the orientational distortions induced in NLC by a suspended object—an individual particle of a suspension. In the rigid anchoring approximation this question had been in detail addressed in Ref. [1], but now we are interested in solutions for the case of finite W values.

Consider a solid acircular particle embedded in a uniform nematic domain whose director $\boldsymbol{n}_0 = \text{const}(\boldsymbol{r})$ is fixed at infinity. We assume that all over the particle surface some definite boundary condition holds. Since the length L of the magnetic grain is always much greater than the NLC molecule size, the particle may be treated as a macroscopic object interacting with the director field via orientational-elastic and surface potentials. The total free energy of the system is then the sum of the corresponding contributions integrated over the sample volume V and the particle surface S, respectively:

$$\mathscr{F} = \frac{1}{2}\left[K \int_V (\nabla \boldsymbol{n})^2 dV + W \int_S \sin^2 \gamma dS \right]. \tag{2}$$

Here γ is the angular deviation of the director from its easy-orientation direction on S. Note that writing down Equation (2) we have made certain conventional simplifications: chosen the surface potential of NLC in the Rapini form (see Refs. [11, 7]), and adopted the single-constant approximation for the elastic energy, i.e., neglected the differences between the Frank moduli K_i setting $K_1 = K_2 = K_3 = K$.

According to usual rules,[11] variation of the functional (2) gives the equilibrium equation for the liquid crystal orientation accompanied by the corresponding boundary condition:

$$\nabla^2 \boldsymbol{n} = 0, \qquad \delta \mathscr{F}|_S = 0, \tag{3}$$

where $\delta \mathscr{F}|_S$ is the variation of $\mathscr{F}$ on the particle surface. At distances $r \gg L$, i.e., far from the particle, the latter but weakly disturbs the orientation field. So the solution of Equation (3) may be presented in the form $\boldsymbol{n}(\boldsymbol{r}) = \boldsymbol{n}_0 + \delta \boldsymbol{n}(\boldsymbol{r})$, where $\delta \boldsymbol{n} = (\delta n_x, \delta n_y, 0)$ in the coordinate system with the z-axis along $\boldsymbol{n}_0$. Taking into account the transversality of the perturbation ($\delta \boldsymbol{n} \perp \boldsymbol{n}_0$), one may write it as

$$\delta \boldsymbol{n} = (\boldsymbol{\Omega} \times \boldsymbol{n}_0), \tag{4}$$

thus introducing an auxiliary pseudo-vector $\boldsymbol{\Omega}$. According to Equations (3–4), it has to satisfy the conditions $\nabla^2 \Omega_x = \nabla^2 \Omega_y = 0$ or the vector Laplace equation

$$\nabla^2 \boldsymbol{\Omega} = 0, \tag{5}$$

everywhere inside the liquid crystal volume.

For a non-chiral particle, vector $\boldsymbol{\Omega}$, vanishing at infinity, expands into inverse power series in r as

$$\boldsymbol{\Omega} = (q/r)\boldsymbol{a} + O(1/r^2), \tag{6}$$

where $\boldsymbol{a}$ and q do not depend upon r. We suppose that the scalar parameter q is determined by the nature of the boundary condition on the particle surface and vector $\boldsymbol{a}$—by the orientation of the particle relative to the liquid crystal. Then for $\boldsymbol{a}$ we may use

the proposed in Ref. [1] representation

$$\boldsymbol{a} = (\boldsymbol{n}_0 \times \boldsymbol{u})(\boldsymbol{n}_0 \boldsymbol{u}) \cdot l, \tag{7}$$

where l is a parameter of the dimension of length, and the unit vector $\boldsymbol{u}$ denotes the direction of the main symmetry axis of the particle[1]. In the following it is convenient to choose l positive, and describe the possible change of vector $\boldsymbol{\Omega}$ direction by the change of sign of q. To comply with the choice (7) of $\boldsymbol{a}$, the "interfacial" coefficient q should be a dimensionless function of the only dimensionless combination available, namely, the ratio

$$\omega = WR/K,$$

(cf. Equation (1)), of the reference particle size R to the so-called extrapolation length $b = K/W$ [11] of the liquid crystal. In below we show that for a solid cylinder suspended in a nematic, parameter R coincides with its radius. As to the magnitude of the function $q(\omega)$, it is easy to point out to its limiting values: for rigid anchoring $|q(\infty)| = 1$ (see Ref. [1]), and for entirely degenerated (isotropic) boundary condition $q(0) = 0$. So it looks reasonable to assume that in the intermediate ω range $|q(\omega)| < 1$.

Returning to the solution (4) of the equilibrium equation and substituting therein Equations (6) and (7), one may present it in the form of a long-wave distortion

$$\delta \boldsymbol{n} = \frac{ql}{r}\boldsymbol{s}, \quad \boldsymbol{s} = (\boldsymbol{n}_0 \boldsymbol{u})(\boldsymbol{n}_0 \times (\boldsymbol{u} \times \boldsymbol{n}_0)). \tag{8}$$

To understand the meaning of vector $\boldsymbol{s}$, let us consider it under condition of small rotations of the particle $|\delta \boldsymbol{u}| = |\boldsymbol{u} - \boldsymbol{u}_0| \ll 1$ for two possible types of the particle equilibrium orientation. At $\boldsymbol{n}_0 \parallel \boldsymbol{u}_0$ and $\delta \boldsymbol{u} \perp \boldsymbol{n}_0$, that is the case addressed in Ref. [1], we get

$$\boldsymbol{s} = \boldsymbol{u} - \boldsymbol{n}_0(\boldsymbol{n}_0 \boldsymbol{u}) = \boldsymbol{u}_\perp,$$

where $\boldsymbol{u}_\perp$ is the component of $\boldsymbol{u}$ in the direction perpendicular to $\boldsymbol{n}_0$ and $\boldsymbol{u}_0$. Since in this situation $\boldsymbol{u}_\perp$ is the whole perturbation, it means that $\boldsymbol{s} = \delta \boldsymbol{u}$. At $\boldsymbol{n}_0 \perp \boldsymbol{u}_0$ which, as it would be shown below, is the case for FN with soft anchoring, expansion of $\boldsymbol{s}$ with respect to small rotations gives

$$\boldsymbol{s} = \boldsymbol{u}_0(\boldsymbol{n}_0 \boldsymbol{u}).$$

The latter vector has, as it ought to, the length $|\delta \boldsymbol{u}|$ but is parallel to $\boldsymbol{u}_0$ which is now the axis along the $\delta \boldsymbol{n}$ direction. From Equation (8) it is clear also that at rigid anchoring

[1] We remark that in general, instead of a mere product $(\boldsymbol{n}_0 \boldsymbol{u})l$, in Equation (7) one has to write $f(\cos \vartheta)$, where f is some odd function of the argument $\boldsymbol{n}_0 \boldsymbol{u} \equiv \cos \vartheta$. The purpose of the simplification made, which in fact is the first term of an expansion of $f(\cos \vartheta)$ in a power series, is that for the problems in question it eventually suffices to provide all the results we are after.

($|q| = 1$) the role of the distortion amplitude is played solely by l while at finite ω, this value is reduced by factor q.

Now one is able to evaluate the torque exerted on the nematic by the embedded particle with an arbitrary orientation $\boldsymbol{u}$. Let us surround the particle by a closed surface Σ sufficiently remote to allow the use of the asymptotic formulae (6) and (8) for $\boldsymbol{\Omega}$ and $\delta\boldsymbol{n}$. Varying the system free energy (2) and taking into account the equilibrium volume and boundary conditions, we get

$$\delta\mathcal{F} = K\int_{\Sigma} d\Sigma_i \delta n_k \partial_i n_k.$$

With the aid of Equation (8) and the transversality condition $\delta\boldsymbol{n} \perp \boldsymbol{n}_0$, it transforms into

$$\delta\mathcal{F} = qKl\boldsymbol{s}\delta\boldsymbol{n}\int_{\Sigma} d\Sigma_i \partial_i\left(\frac{1}{r}\right) = -4\pi qKl\boldsymbol{s}\,\delta\boldsymbol{n}.$$

Hence, the torque exerted on the nematic by the particle may be written as

$$\boldsymbol{\Gamma} = -\boldsymbol{n}\times\frac{\delta\mathcal{F}}{\delta\boldsymbol{n}} = 4\pi qKl(\boldsymbol{n}_0\boldsymbol{u})(\boldsymbol{n}_0\times\boldsymbol{u}). \tag{9}$$

If the particle does not experience any additional external force (magnetic, gravitational, etc.), then its torque-free static orientation $\boldsymbol{u}_0$ is determined by condition $\boldsymbol{\Gamma} = 0$. Equation (9) provides two choices, viz. $\boldsymbol{u}_0 \parallel \boldsymbol{n}_0$ and $\boldsymbol{u}_0 \perp \boldsymbol{n}_0$. Of the latter, the stable one is selected by the demand that the free energy decrement should be positive, or that the perturbation-induced torque of the nematic matrix should restore the initial state. From Equation (9), it follows that the actual equilibrium orientation of the particle is determined by the sign of the coefficient q. For example, at $q > 0$ it is stable at $\boldsymbol{u}_0 \parallel \boldsymbol{n}_0$ and unstable at $\boldsymbol{u}_0 \perp \boldsymbol{n}_0$. Note that neither of these two orientations induce any long-wave distortion: substitution of Equation (7) into Equation (9) at $\boldsymbol{\Gamma} = 0$ yields $\boldsymbol{a} = 0$. So, these distortions do really exist only when there is some external torque $\boldsymbol{\Gamma}_{ext}$ acting on the particle. In equilibrium, $\boldsymbol{\Gamma}_{ext}$ is counteracted by the torque $-\boldsymbol{\Gamma}$ exerted by the nematic on the particle, and the balance condition gives $\boldsymbol{a} = \boldsymbol{\Gamma}_{ext}/4\pi qK$.

3 EVALUATION OF DISTORTION ENERGY FOR A CYLINDRICAL PARTICLE

We are considering a particle in the form of a long cylinder (its length being L and diameter $2R \sim L/10$) suspended in NLC and assume that the boundary conditions are the same all over the cylinder surface. Let us evaluate the free energy (2) for an arbitrary orientation of the particle axis relative to the unperturbed director $\boldsymbol{n}_0$. Though the exact solution of this problem could be found only for certain particular cases,[5] it is feasible to obtain a reasonable approximation for the general one. For this purpose, we need to estimate the volume and surface integrals entering Equation (2). Doing that, we shall neglect the effect of the end-walls of the cylinder, since their contributions are about d/L times less than that of the lateral surface. Taking into account that in the case of finite

anchoring $|\nabla \boldsymbol{n}| \sim 1/b$ near the particle surface, for the contribution of the orientational-elastic term we have

$$\tfrac{1}{2}K \int_V (\nabla \boldsymbol{n})^2 dV \sim \pi K L R^2 (W/K)^2 = \omega^2 \cdot \pi K L, \tag{10}$$

and for the second term of Equation (2)

$$\tfrac{1}{2}W \int_S \sin^2 \gamma \, dS \sim \pi W R L = \omega \cdot \pi K L. \tag{11}$$

Comparison of Equations (10) and (11) shows that up to the first order of magnitude in parameter $\omega = WR/K \ll 1$ (cf. Equation (1)) the free energy may be replaced merely by its surface term. We would like to remark that though the contribution of volume distortions to the free energy is neglected here, the above-derived formula (8) is essential for explanation of the collective behavior of FN—see Sec. **3**.

Following approximation $\omega < 1$, let us write the director on the particle surface as $\boldsymbol{n}_S = \boldsymbol{n}_0 + \delta \boldsymbol{n}_S$, where $|\delta \boldsymbol{n}_S| \sim \omega$. Since the surface angle γ entering Equations (2) and (11) is defined by relation $\sin\gamma = (\boldsymbol{n}_{0S} \times \boldsymbol{n}_S)$, where $\boldsymbol{n}_{0S}$ is the direction of easy orientation on the particle surface, with the same accuracy we may set $\sin \gamma = (\boldsymbol{n}_{0S} \times \boldsymbol{n}_0)$ and thus present the free energy of the particle-induced distortion in the form

$$\mathscr{F} = \tfrac{1}{2}W \int_S (\boldsymbol{n}_{0S} \times \boldsymbol{n}_0)^2 dS. \tag{12}$$

In the cylindrical coordinate framework fixed on the particle, vectors $\boldsymbol{n}_0$ and $\boldsymbol{n}_{0S}$ may be written as

$$\begin{aligned} \boldsymbol{n}_0 &= (\sin\theta, 0, \cos\theta), \\ \boldsymbol{n}_{0S} &= (\sin\alpha\cos\beta, \sin\alpha\sin\beta, \cos\alpha), \end{aligned} \tag{13}$$

where the angles are defined in Figure 1. Substituting Equations (13) into Equation (12), one gets after integration

$$\mathscr{F} = \tfrac{1}{2}\pi\omega K L[1 + \cos^2\alpha - (3\cos^2\alpha - 1)\cos^2\theta]. \tag{14}$$

Differentiation with respect to θ yields the expression for the torque exerted by the particle on the nematic. With the notation $\cos\theta = (\boldsymbol{n}_0 \boldsymbol{u})$—see Figure 1—it takes the form

$$\boldsymbol{\Gamma} = \pi\omega K L(3\cos^2\alpha - 1)(\boldsymbol{n}_0 \boldsymbol{u})(\boldsymbol{n}_0 \times \boldsymbol{u}), \tag{15}$$

which justifies the choice of the auxiliary vector $\boldsymbol{a}$ in Equation 7. Comparing Equations (9) and (15) we see that for soft anchoring ($\omega < 1$) the distortion amplitude l and the

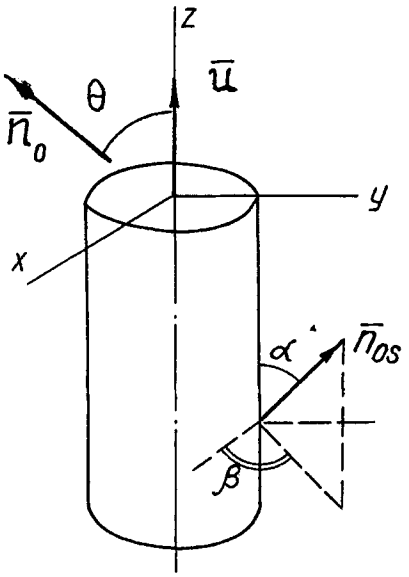

FIGURE 1 Cylindrical particle suspended in a nematic; on the choice of the reference angles. Here $\boldsymbol{u}$ is the unit vector of the particle major axis, $\boldsymbol{n}_0$ is the unperturbed director of the nematic domain, $\boldsymbol{n}_{0S}$ is the easy orientation direction on the particle surface, α and β are the angles of $\boldsymbol{n}_{0S}$ with the axes of the coordinate framework whose polar axis lies along $\boldsymbol{u}$.

"interfacial" coefficient q may be chosen, respectively, as

$$l = L, \quad q = \tfrac{1}{2}\omega P_2(\cos\alpha), \tag{16}$$

where P_2 $(\cos\alpha)$ is the second-order Legendre polynomial. Note that the angle α depends solely on the kind of the boundary condition and for a given material triad *particle substance-surfactant-nematic* may be only but temperature dependent.

The obtained expression for q is useful, in particular, to determine the type of the particle equilibrium orientation. Writing down the difference between the particle energies (14) in the orthogonal orientations, viz. $\boldsymbol{u} \parallel \boldsymbol{n}_0$ and $\boldsymbol{u} \perp \boldsymbol{n}_0$, one gets

$$\Delta\mathcal{F} = \mathcal{F}_{\parallel} - \mathcal{F}_{\perp} = -2\pi q K L. \tag{17}$$

This formula provides a straightforward way of selection of the stable equilibrium states of the particle. From there it is apparent that it is the sign of the coefficient q, i.e., the orientational pattern of anchoring, which determines the type of equilibrium. As Equations (16) show, the sign of q is controlled by the angle α between the easy-orientation direction $\boldsymbol{n}_{0S}$ and the symmetry axis of the cylinder—see Figure 1 for definition of α. Introducing the reference value $\alpha_* = \arccos(1/\sqrt{3})$ whence $P_2(\cos\alpha_*) = 0$, we find that

$$\begin{aligned} &\Delta\mathcal{F} < 0 \quad \text{and} \quad \boldsymbol{u} \parallel \boldsymbol{n}_0 \quad \text{for} \quad \alpha < \alpha_*, \\ &\Delta\mathcal{F} > 0 \quad \text{and} \quad \boldsymbol{u} \perp \boldsymbol{n}_0 \quad \text{for} \quad \alpha > \alpha_*. \end{aligned} \tag{18}$$

Note also that with the aid of formula (17) one may rewrite the orientational energy of the particle (14) as

$$\mathscr{F}(\theta) = \mathscr{F}_\perp + [\mathscr{F}_\parallel - \mathscr{F}_\perp](\boldsymbol{u}\boldsymbol{n}_0)^2 \quad \mathscr{F}_\perp = -2\mathscr{F}_\parallel = 4\pi qKL/3. \tag{19}$$

It is clear that the existence of a definite preferred orientation of a particle in a nematic matrix is the necessary condition for establishing the orientational coupling in a system like FN. However, the results of Equations (18) are valid only if the energy gap $|\Delta\mathscr{F}|$ is greater than the thermal energy k_BT, i.e.,

$$WRL/k_BT \gg 1.$$

Substituting here the reference values of the material parameters of thermotropic FN, we find that at room temperature $WRL/k_BT \sim 10$–100. But this condition might break down for too small particles or too low surface energies.

4 COLLECTIVE BEHAVIOR OF THE PARTICLES

Now we proceed to the question of the orientational coupling between the nematic and the particle assembly suspended in it. As it had been shown in Ref. [1], in the systems alike FN, the nematic matrix in response to the unison rotation of the particles might display two types of the orientational behavior. The first one occurs when the number concentration c of the solid phase is lower than some characteristic value c_*. Under these circumstances each particle distorts the director field independently of the neighbors, and the deviations between $\boldsymbol{u}$ and local $\boldsymbol{n}$ are great. Hence, the resulting perturbations but weakly influence the macroscopic structure of the nematic. Conversely, if the particle concentration exceeds c_*, then the response mode known as *the collective behavior*[1] takes place. In the collective behavior, the local orientation deviations of the particles and nematic are close and change smoothly all over the FN sample volume. Only in this case the rotation of particles produces a substantial macroscopic orientational response in the NLC matrix. Let us use the method proposed in Ref. [1] to evaluate the critical value c_* in the case of finite surface energies W.

Consider an assembly of cylinder-like particles in a nematic with the initially uniform director $\boldsymbol{n}_0$. Let vector $\boldsymbol{r}_p$ denote the position of the centre of mass for the p-th particle and unit vector $\boldsymbol{u}_p$—its symmetry axis direction. As formerly, we assume that the deviations of the particle orientation from its equilibrium direction are small: $|\delta\boldsymbol{u}| \ll 1$. With allowance for Equations (8) and (16) the volume distortions of the director field may be presented in the form

$$\delta\boldsymbol{n}(\boldsymbol{r}) = \sum_p \frac{qL}{|\boldsymbol{r} - \boldsymbol{r}_p|}[\delta_u\boldsymbol{s} + \delta_n\boldsymbol{s}]_p, \tag{20}$$

where the term in square brackets is the sum of partial variations of the vector $\boldsymbol{s}$ from Equation (8) with respect to $\boldsymbol{u}$ and $\boldsymbol{n}_0$ taken at the point $\boldsymbol{r}_p$. The meaning of such a form

of the right-hand side of Equation (20) becomes clear if to write it explicitly for the cases of parallel and perpendicular orientations of the particles. As it has been shown in Sec. **2**, at $q > 0$ the equilibrium state is $\boldsymbol{u}_0 \parallel \boldsymbol{n}_0$. Taking the corresponding variations of $\boldsymbol{s}$, we get

$$\delta_u \boldsymbol{s} = \boldsymbol{u}_\perp, \qquad \delta_n \boldsymbol{s} = -\delta \boldsymbol{n};$$

both functions are defined at the point $\boldsymbol{r}_p$. Substitution to Equation (20) yields

$$\delta \boldsymbol{n}(\boldsymbol{r}) = \sum_p \frac{qL}{|\boldsymbol{r} - \boldsymbol{r}_p|} [\boldsymbol{u}_\perp - \delta \boldsymbol{n}]_p, \tag{21}$$

and grants that a grain positioned in $\boldsymbol{r}_p$ causes no distortions if it aligns with the local director $\boldsymbol{n} = \boldsymbol{n}_0 + \delta \boldsymbol{n}(\boldsymbol{r}_p)$.

For the case $\boldsymbol{u}_0 \perp \boldsymbol{n}_0$ when the parameter q is negative, the pertinent variations give

$$\delta_u \boldsymbol{s} = \boldsymbol{u}_0 (\boldsymbol{n}_0 \boldsymbol{u}), \qquad \delta_n \boldsymbol{s} = \boldsymbol{u}_0 (\boldsymbol{u}_0 \delta \boldsymbol{n}).$$

With the use of these formulae, Equation (20) transforms into

$$\delta \boldsymbol{n}(\boldsymbol{r}) = \sum_p \frac{qL}{|\boldsymbol{r} - \boldsymbol{r}_p|} [(\boldsymbol{n}_0 \boldsymbol{u}) + (\boldsymbol{u}_0 \delta \boldsymbol{n})]_p. \tag{22}$$

Here the role of the right-hand side term proportional to $\delta \boldsymbol{n}$ is the same as in Equation (21)—to eliminate long-range distortions if the director field in $\boldsymbol{r}_p$ has the form exactly fitting the particle orientation $\boldsymbol{u}$. However, due to a more complicated relation between $\boldsymbol{n}_0$ and $\boldsymbol{u}_0$, the structure of the bracket content in Equation (22) is much less obvious than that of (21).

To pass to the continual description, let us act upon Equation (20) with the spatial Laplace operator ∇^2. This yields the equation

$$\nabla^2 \delta \boldsymbol{n} = -4\pi c q L (\delta_u \boldsymbol{s} + \delta_n \boldsymbol{s}), \tag{23}$$

where c is the number concentration of the particles.

With the use of the above-obtained expressions for $\delta \boldsymbol{s}$ we reduce Equation (23) in the considered particular cases to

$$\nabla^2 \delta \boldsymbol{n} = -\xi^2 (\boldsymbol{u}_\perp - \delta \boldsymbol{n}), \qquad \text{for } \boldsymbol{n}_0 \parallel \boldsymbol{u}_0,$$

$$\nabla^2 (\boldsymbol{u}_0 \delta \boldsymbol{n}) = \xi^2 [(\boldsymbol{n}_0 \delta \boldsymbol{u}) + (\boldsymbol{u}_0 \delta \boldsymbol{n})], \quad \text{for } \boldsymbol{n}_0 \perp \boldsymbol{u}_0,$$

where

$$\xi^2 = 4\pi c |q| L. \tag{24}$$

Both equations have the same formal solution

$$\Phi(\boldsymbol{r}) = c|q|L \int d\boldsymbol{r}' \frac{\exp(-\xi|\boldsymbol{r}-\boldsymbol{r}'|)}{|\boldsymbol{r}-\boldsymbol{r}'|} \Psi(\boldsymbol{r}'), \tag{25}$$

where $\Phi = \delta\boldsymbol{n}$ and $\Psi = \boldsymbol{u}_\perp$ for the parallel case, and $\Phi = (\boldsymbol{u}_0 \delta\boldsymbol{n})$ and $\Psi = -(\boldsymbol{n}_0 \delta\boldsymbol{u})$ for the perpendicular one. The structure of the kernel in Equation (25) shows that a distortion arisen by an individual particle is screened out (due to the presence of the other particles) at distances greater than ξ^{-1}. Setting $c \sim 10^{10}\,\mathrm{cm}^{-3}$ and taking $q \sim 10^{-1}$ (soft anchoring), one finds $\xi^{-1} \sim 10\,\mu\mathrm{m}$ as the reference value.

Assume that inside some region (its size being D) of the FN sample a unison rotation $\delta\boldsymbol{u} \neq 0$ of the particles is induced, while elsewhere $\delta\boldsymbol{u} = 0$. In this case the estimation of the integral of Equation (25) for the points inside the region of rotation gives

$$\Phi \sim [1 - \exp(-D\xi)]\Psi.$$

It shows that the degree of orientation imposed by the particles on the director field, is determined by the ratio of the specimen size to the screening length ξ^{-1}. For $D \gg \xi^{-1}$ the director distortions are substantial ($|\delta\boldsymbol{n}| \approx |\delta\boldsymbol{u}|$), i.e., the particles govern the macroscopic texture of the nematic. In the opposite case $D \ll \xi^{-1}$ the particle-induced director perturbations are minor ($|\delta\boldsymbol{n}| \ll |\delta\boldsymbol{u}|$) and, therefore, macroscopically negligible.

From the definition of ξ, see Equation (24), it follows that to achieve the collective response, the particle concentration at given D must exceed the critical value

$$c_* \sim (|q|LD^2)^{-1}. \tag{26}$$

In the rigid anchoring limit ($q = 1$) this estimate coincides with that obtained in Ref. [1]: $c_* \sim (LD^2)^{-1}$. For the finite anchoring, c_* becomes q^{-1} times larger due to the renormalization of the distortion amplitude: $L \to |q|L$. The scale dependences $c_* \propto (LD^2)^{-1}$ had been confirmed in Ref. [12] by measurements on lyotropic FN.

As a matter of fact, the origin of the critical concentration c_* may be explained on the basis of very simple considerations. Let us compare the energies associated with the two possible modes of response of the NLC matrix to a unison rotation of the particles. The first mode is the *individual behavior*, when each particle distorts the matrix independently on the others. The energy of such a non-uniformity, according to formula (11) is $\sim \omega KL$ per particle. For a unit volume containing c particles, it is $E_{\mathrm{ind}} \sim c\omega KL$. The second mode, which is the collective response, takes place when the particles are oriented relatively to the director by almost equilibrium angle, and the director distortions are smeared down over the largest spatial scale available, i.e., the specimen size D. For this case the orientational-elastic contribution to the energy density is $E_{\mathrm{coll}} \sim K|\nabla\boldsymbol{n}|^2 \sim K/D^2$. Apparently, the actual mode of response would be the one with the lower energy increment. Comparison of E_{ind} and E_{coll} shows that the collective mode is favored as soon as

$$c \geq 1/\omega LD^2.$$

Recalling that the "interfacial" parameter q by the order of magnitude equals to ω, see formula (16), we immediately recover the relation (26).

If to measure the particle concentration in the units of the dimensionless volume fraction $f = cv$, where v is the particle volume, then for the assembly of cylindrical particles one gets with the aid of Equations (16) and (26) the lower bound of the collective behavior in the form $f_* = c_* v \sim (bd/D^2)$. Taking for estimates a thermotropic FN sample (layer) with $D \sim 100\,\mu m$, $d \simeq 70\,nm$ and $b \sim 100\,nm$, we find $f_* \leq 10^{-6}$. This ensures that the amount of the ferromagnetic admixture sufficient to acquire control over the NLC texture, is rather small.

5 COMPENSATED AND MAGNETIZED FERRONEMATICS

Magnetic properties of FN are the "sum" of contributions from the nematic matrix and ferroparticles. The nematic itself provides the well-known diamagnetic term[11] which at $f \ll 1$ does not depend upon the presence of the particles, and further on would be treated as usual. Getting acquainted with the other one, needs to consider the orientation of the particles. Each single-domain prolate grain made of a ferromagnetic material with the saturation magnetization M_s, bears the permanent magnetic moment $\boldsymbol{\mu} = M_s v \boldsymbol{u}$, where $\boldsymbol{u}$ denotes the unit vector of the particle major axis. According to relations (18), in a uniform nematic with the director $\boldsymbol{n}_0$ such particles settle either along (at $\alpha < \alpha_*$) or transversely (at $\alpha > \alpha_*$) to the optical axis of the matrix. Hence, in the first case the magnetic moments with equal probability acquire directions $\boldsymbol{n}_0$ or $-\boldsymbol{n}_0$, whereas in the second case—are oriented in an arbitrary way but in the planes normal to $\boldsymbol{n}_0$. In other words, depending upon the boundary angle α, the nematic environment (the NLC matrix) creates for the particles the anisotropy either of the "easy-axis" or "easy-plane" type.

In the absence of the external field or without special preparations these systems are expected to dwell in a magnetically compensated state, where their magnetization $\boldsymbol{M} = (1/\Delta V)\Sigma \boldsymbol{\mu}_i$, i.e., the sum of magnetic moments averaged over a macroscopically infinitesimal volume element ΔV, is zero. However, to be able to govern the FN texture, one needs the suspension with a non-zero initial ("spontaneous") magnetization. For FN whose particles align with the director there exist at least two ways to achieve such a state, see Ref. [1]. Namely, they are:

—the system is cooled from the isotropic phase down to the nematic one in the presence of a uniform magnetic field $\boldsymbol{H}$ parallel to the would-be optical axis of the nematic. (This direction might be determined, for example, by the boundary conditions on the sample walls.) In the isotropic state the particles align their magnetic moments with $\boldsymbol{H}$, and the temperature-induced transition in the nematic matrix traps this configuration so that it continues to exist after the removal of the field;

—the already prepared compensated FN sample is subjected to a single short magnetic field pulse with the amplitude $H > H_c$, where $H_c \simeq 2\pi M_s$ is the particle coercive force. If the duration of the pulse is shorter than the characteristic time of the particle mechanical rotation, then, due to the intraparticle flip of the magnetic

moments over the potential barrier of magnetic anisotropy, all the magnetic moments of the particles in a suspension align along the same direction. After this tuning up, the magnetization of FN is fixed by the orientational coupling ($\pi qKL \gg k_B T$). The effective internal field, stabilizing this "spontaneous" magnetization, is $H_a \sim \pi qKL/M_s v = 4Kq/M_s d^2$. For $q = 0.1$, $K = 5 \cdot 10^{-7}$ dyn, $M_s = 500$ G and $d = 7 \cdot 10^{-6}$ cm the estimate yields $H_a \sim 10$ Oe.

Now let us consider a ferronematic with rod-like particles lying in the planes perpendicular to the axis of the nematic. In this situation the previous estimate for the stabilizing field strength H_a holds as well. But due to the different kind of its symmetry, $\boldsymbol{H}_a$, however perfectly suppressing the deviations of the particles from the singled-out plane, cannot build up a magnetized state. To create and maintain a non-zero magnetization, such a system should be subjected to a certain external field $\boldsymbol{H}_b \perp \boldsymbol{n}_0$. Rotation of ferroparticles to the direction of $\boldsymbol{H}_b$ does not distort the equilibrium texture of the nematic matrix, and FN magnetizes like a two-dimensional isotropic paramagnet:

$$M = M_s f I_1(\rho)/I_0(\rho). \tag{27}$$

Here f is the local value of the solid phase volume fraction, I_1 and I_0 are the modified Bessel functions of the so-called Langevin parameter $\rho = M_s v H_b / k_B T$, which is the ratio of the magnetic energy of the particle to the energy of its thermal motion. The asymptotics of formula (27) are

$$M = M_s f \begin{cases} \rho/2, & \text{for } \rho \ll 1, \\ 1 - 1/2\rho, & \text{for } \rho \gg 1, \end{cases}$$

so that the saturation behavior $M \to M_s f$ at $\rho \gg 1$ is clear. Using the cited above dimensional data, one finds that $\rho \geq 10$ at room temperature for the field strength as small as $H \leq 1$ Oe. Hence, even a weak field, lying in the "easy plane", makes FN to be magnetized nearly perfectly.

Further on we shall deal only with the magnetized FN, so it is convenient to describe their macroscopic magnetization distribution by a unit vector $\boldsymbol{m}(\boldsymbol{r})$ defined by relation

$$\boldsymbol{M} = M_s f \boldsymbol{m}(\boldsymbol{r}), \tag{28}$$

where the averaging over the volume element $\Delta V \gg L^3$ is implied. Having once adopted relation (28), we take for granted that FN is locally saturated. For rigid anchoring, as in Ref. [1], formula (28) immediately reduces to $\boldsymbol{M} = M_s f \boldsymbol{n}$. For the case of soft anchoring Equation (28) must be taken in its initial form. One has just to remember that in this case the basic state of FN is not completely field-free, but includes a certain small uniform bias field $\boldsymbol{H}_b$ fixing the direction of $\boldsymbol{m}$ inside the "easy plane". In any applied field $\boldsymbol{H}$, the resulting distribution $\boldsymbol{m}(\boldsymbol{r})$ is determined by the joint action of $\boldsymbol{H} + \boldsymbol{H}_b$. As it has been shown in above, the reference value of H_b is tiny; in the experiments [4, 8–10] it had been demonstrated that as $\boldsymbol{H}_b$ is convenient to employ the terrestrial magnetic field (~ 0.5 Oe).

6 FREE ENERGY DENSITY OF A FERRONEMATIC

To solve any macroscopic problems concerning ferronematics, one needs to have the pertinent free energy expression. The corresponding formula for the soft-anchoring case follows from the above presented considerations and reads

$$F = \tfrac{1}{2}[K_1(\operatorname{div}\boldsymbol{n})^2 + K_2(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n})^2 + K_3(\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n})^2] - \tfrac{1}{2}\chi_a(\boldsymbol{nH})^2$$

$$- M_s f(\boldsymbol{mH}) + (fk_BT/v)\ln f + (AWf/d)(\boldsymbol{nm})^2, \tag{29}$$

Having written down its complete form, now let us explain its strucutre. The first bracket represents the standard Frank potential of the nematic matrix, K_i being the orientation-elastic moduli. The second term is also well-known, and yields the density of the magnetic energy of the nematic matrix, where χ_a stands for the anisotropic part of the NLC diamagnetic susceptibility; for all usual nematics χ_a is positive. The next two terms of Equation (29) represent the magnetic energy of ferroparticles in the external field, transformed via Equation (28), and the contribution of the mixing entropy of the their ideal solution, respectively. The last term of Equation (29) is more peculiar and needs clarification. Returning to Equation (19) for the energy of the individual particle in the soft-anchoring limit, we may rewrite its part depending on the particle orientation as

$$\mathscr{F}(\theta) = (AWv/d)(\boldsymbol{un}_0)^2, \tag{30}$$

where parameter $A = -2P_2(\cos\alpha)$, see Equations (14)–(16), is determined by the type of the boundary condition. It is reasonable to assume that for an orientationally-deformed magnetized FN this equation holds as well, if to replace $\boldsymbol{u}\to\boldsymbol{m}$ and $\boldsymbol{n}_0\to\boldsymbol{n}$. Proceeding to the macroscopic scale and multiplying Equation (30) by the particle concentration c, we recover the particle-matrix interaction term entering Equation (29). For homeotropic orientation one has $\alpha = \pi/2$, see Figure 1, and thus $A = 1$.

The proposed continuum expression (29) is specified to describe FN with weak ($\omega < 1$) orientational coupling. According to it, the state of FN is characterized by three thermodynamically-independent spatial distributions, viz. director $\boldsymbol{n}(\boldsymbol{r})$, particle concentration $f(\boldsymbol{r})$ and unit vector of magnetization $\boldsymbol{m}(\boldsymbol{r})$. It is worth to remind that the model of Ref. [1], that takes for granted the rigid anchoring of NLC on the particles, prescribes the unbreakable relation $\boldsymbol{m}(\boldsymbol{r}) = \boldsymbol{n}(\boldsymbol{r})$, thus eliminating $\boldsymbol{m}(\boldsymbol{r})$ from consideration. Note, however, that the same result follows as well from Equation (29) after the limiting transition $W\to\infty$ at $A < 0$.

7 BONDING EQUATION AND SEGGREGATION EFFECT IN A FERRONEMATIC

Integrating the free-energy density (29) over the volume of the FN sample, we get the total energy in the form of a functional $\tilde{\mathscr{F}} = \int F\,dV$. Its minimization with respect to

$\boldsymbol{m}(\boldsymbol{r})$ yields the equation for the equilibrium magnetization

$$(\boldsymbol{m} \times \boldsymbol{H}_e) = 0, \tag{31}$$

where the effective field governing the orientation of magnetic particles in FN is

$$\boldsymbol{H}_e = -\delta\tilde{\mathscr{F}}/\mu\delta\boldsymbol{m} = \boldsymbol{H} + H_a(\boldsymbol{mn})\boldsymbol{n}, \quad H_a = -2AW/M_s d. \tag{32}$$

These formulae show that the spatial distribution of the magnetization direction $\boldsymbol{m}(\boldsymbol{r})$ depends upon both the external field $\boldsymbol{H}$ and the internal, parallel to the director, anisotropy field $\boldsymbol{H}_a$. In the equilibrium state the vector triad $\boldsymbol{H}, \boldsymbol{m}$, and $\boldsymbol{n}$ should be coplanar in each point of the sample. At given $\boldsymbol{H}$, Equation (31) with allowance for Equation (32) couples the orientational distributions $\boldsymbol{m}(\boldsymbol{r})$ and $\boldsymbol{n}(\boldsymbol{r})$ thus modifying the rigid anchoring model. With regard to this fact, further on we shall refer to Equation (31) as *the bonding equation*. In scalar representation it reads

$$H_a \sin 2\theta = 2H \sin(\chi - \theta),$$

where the angles are defined in Figure 2.

Note that Equations (31)–(32) closely resemble (in fact, coincide with) those describing the equilibrium orientation of the magnetic moment in a single-domain magnetic crystal with a uniaxial anisotropy (see Ref. [13], for example). In the latter case the orientation-dependent part of the particle energy is

$$U = -M_s v(\boldsymbol{mH}) - K_a v(\boldsymbol{mv})^2,$$

where K_a is the magnetic anisotropy constant and $\boldsymbol{v}$ is the unit vector of the magnetic anisotropy axis direction. If to fix the sample orientation, i.e., vector $\boldsymbol{v}$, then the equilibrium direction of the magnetic moment $\boldsymbol{m}$ is determined by minimization of U with respect to $\boldsymbol{m}$. This yields exactly Equations (31) and (32) where now $H_a = 2K_a/M_s$. This means that in FN the nematic matrix is the source of the uniaxial anisotropy field acting on the ferroparticles, $-AW/d$ being the anisotropy constant. This effective field singles out the preferable directions and stabilizes the remanence magnetization of FN. As long as the external field is weak ($H \ll |H_a|$), ferroparticle orientation is governed by the director. Since in real FN the amplitude H_a is about 10 Oe, it means that the particle coupling with the NLC matrix might be considered as "rigid" only if $H \geq 1$ Oe. In the opposite limiting case ($H \gg |H_a|$), i.e., $H \gg 10^2$ Oe, the particle orientation is controlled by the applied field.

Now let us evaluate the equilibrium distribution of the particle concentration. Minimization of the functional $\tilde{\mathscr{F}}$ with respect to $f(\boldsymbol{r})$ gives the Boltzmann-like formula

$$f = f_0 \exp\left[\frac{M_s v}{k_B T}(\boldsymbol{mH}) - \frac{AWv}{k_B T d}(\boldsymbol{nm})^2\right], \tag{33}$$

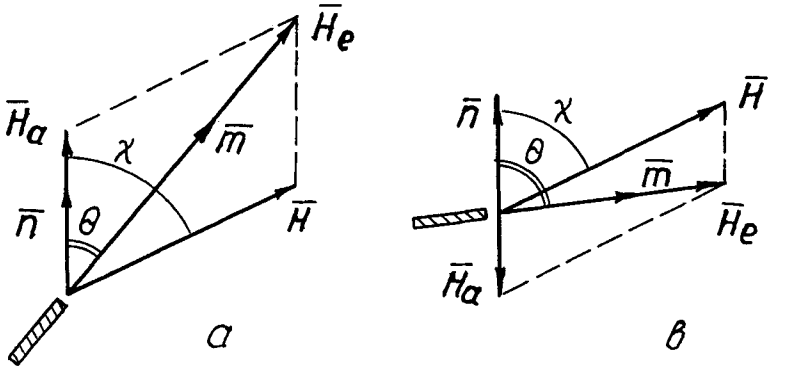

FIGURE 2 On the definition of the effective magnetic field acting on the magnetization of FN for the cases of positive (*a*) and negative (*b*) anisotropy. Note that the dashed rod is drawn only as an eye guide, all the presented vectors are the variables of the macroscopic model.

where the constant f_0 is determined by the usual normalizing condition

$$\int_V f(\boldsymbol{r})dV = N,$$

fixing the total number N of the particles.

At $\boldsymbol{H}=0$ vector $\boldsymbol{m}$ according to Equations (31)–(32) is always parallel to the anisotropy field, that means $(\boldsymbol{nm}) = \text{const}\,(\boldsymbol{r})$. This makes Equation (33) trivial, so that it does not affect any initial distribution of concentration. Formula (33) becomes important if it is necessary to analyze the field-induced distribution of the particles in an orientationally deformed FN. Consider a uniform magnetic field $\boldsymbol{H}$ imposed on a non-uniformly oriented sample of FN, where the initial concentration of the particles is constant. Due to the spatial dependence of the orientational texture $\boldsymbol{n}(\boldsymbol{r})$, the power exponent in formula (33) becomes a function of coordinates. It is increased in those regions of the sample where the particles, being in the most favorable orientation relatively to the local director $\boldsymbol{n}(\boldsymbol{r})$ are at the same time most closely aligned with the applied field. Since the distribution (33) is the equilibrium one, we conclude that upon application of the field, the particles move, populating some particular places of the sample, singled out by relative orientation of $\boldsymbol{n}$ and $\boldsymbol{H}$. This equilibrium concentration re-distribution, that, after Ref. [1], is called *the seggregation effect*, is one of the most striking specific features of FN. Note that it is provoked by a uniform field and has nothing to do with the plain magnetophoresis.

CONCLUSION

We have discussed the continuum theory of ferronematics—the unusual anisotropic fluid media firstly proposed by Brochard and de Gennes. Since FN is a heterogeneous substance consisting of at least two interacting phases, each of which is anisotropic, its

correct model could be constructed only after thorough studies on the "microscopic", i.e., of the order of the particle size, spatial scale. The subject of our interest are FN with soft anchoring of the nematic molecules on the particle surfaces. By now this kind of FN is represented by thermotropic systems. Resumé of theoretical estimates and experimental data yields that actually the notion of thermotropic FN implies a suspension of prolate (rod-like) magnetically hard particles magnetized along their long axes. The mean particle dimensions are: length $L \sim 0.1$ μm and diameter $d \sim L/10$; their volume fraction range $f \leq 10^{-4}$. Such systems, once being magnetized, acquire and retain the spontaneous magnetization up to $M \approx M_s f \sim 10^{-1}$ G.

The equilibrium orientational state of FN depends upon the type and strength of anchoring of the NLC molecules on the particle surfaces. For plain nematic carriers, like MBBA, providing the anchoring is homeotropic, it is inevitably soft. Hence, the basic internal structure of such a FN is the one, where director and magnetization vectors are perpendicular to each other. For the latter case we have developed a continual description, i.e., derived the free-energy density function F, see equation (29). This expression formally determines F for arbitrary states (including non-equilibrium ones). Balance relations describing stationary situations are obtained then by minimization of F or functional $\tilde{\mathcal{F}}$ based on it. These two vector and one scalar equations following from relations $\delta\tilde{\mathcal{F}}/\delta \boldsymbol{n} = \delta\tilde{\mathcal{F}}/\delta \boldsymbol{m} = \delta\tilde{\mathcal{F}}/\delta f = 0$, together with the corresponding boundary conditions, form a closed set determining the equilibrium texture of FN. Namely, its orientation $\boldsymbol{n}(\boldsymbol{r})$, magnetization direction $\boldsymbol{m}(\boldsymbol{r})$ and concentration $f(\boldsymbol{r})$ distributions for arbitrary values of the external magnetic field. In the second part of the paper we apply our model to get quantitative results in a number of actual problems of FN behavior.

Acknowledgements

This work was done partially under the auspices of the Russia State Committee on High Education and Science under the grant No. T-32-2, and International Science Foundation under the grant No. RMD 000.

References

1. F. Brochard and P. G. de Gennes, *J. Phys.* (France), **31**, 691 (1970).
2. J. Rault, P. E. Cladis and J. P. Burger, *Phys. Lett. A*, **32**, 199 (1970).
3. L. Liebert and A. Martinet, *J. Phys. Lett.* (France), **40**, L363 (1979).
4. S.-H. Chen and N. M. Amer, *Phys. Rev. Lett.*, **51**, 2298 (1983).
5. S. V. Burylov and Yu. L. Raikher, *Phys. Lett. A*, **149**, 279 (1990).
6. S. V. Burylov and Yu. L. Raikher, *J. Magn. and Magn. Mater.*, **85**, 74 (1990).
7. J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon & Breach), Chap. 2. (1982).
8. S.-H. Chen and S. H. Chiang, *Mol. Cryst. Liquid Cryst.*, **144**, 359 (1987).
9. S.-H. Chen and B. J. Liang, *Optics Lett.*, **13**, 716 (1988).
10. B. J. Liang and S.-H. Chen, *Phys. Rev. A*, **39**, 1441 (1989).
11. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press), Chap. 3. (1974).
12. A. M. Figueiredo Neto and M. M. F. Saba, *Phys. Rev. A*, **34**, 3483 (1986).
13. L. D. Landau and E. M. Lifshitz., *Electrodynamics of Continuous Media* (Pergamon Press), Chap. 5. (1960).