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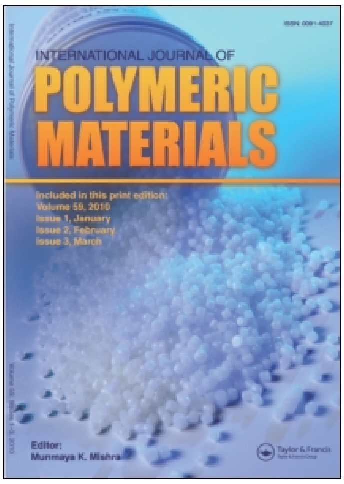

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Orientational and Magnetic Behavior of a Colloidal Magnetic Suspension in a Cholesteric Liquid Crystal Matrix

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Orientational and magnetic properties of a ferrocholesteric, i.e. highly dispersed magnetic suspension in a cholesteric liquid crystal matrix in a magnetic field which is perpendicular to the spiral axes is considered. Two mechanisms of the field influence on the ferrocholesteric are taken into account: the dipolar one due to the interaction between the field and the magnetic moments of the needle-liked particles and the quadrupolar one due to the field influence on the cholesteric matrix. The field influence on the orientational structure, the spiral pitch, the magnetization and the concentration of the magnetic admixture is studied. The dependence of the ferrocholesteric-ferronematic transition critical field on the material parameters of the suspension is found.

KEY WORDS Magnetic, colloidal, suspension, cholesteric, orientation.

1. INTRODUCTION

Ferrocholesterics (FC) are suspensions of ferromagnetic particles with a cholesteric liquid crystal (CLC) as its carrier. Conserving the features of the CLC orientational behavior, these suspensions have the magnetic susceptibility at least some orders of magnitude higher than that for pure CLC. They allow to control their texture by relatively weak magnetic fields.

The solid phase of the FC consists of the mono-domain needle-liked ferromagnetic particles with the length $l >> a$ and the diameter $d \sim l/10$, here a is a molecular length. Strong anizometricity of the particles gives rise to the strong coupling between the magnetic moment and the particle body. Covering the particles by surface-active materials leads to the orientational coupling between their long axes and the local director $\mathbf{n}$. The homogeneous magnetic field $\mathbf{H}$ orients the ferroparticles and then it holds to the distortion of the director field in the CLC matrix. This situation corresponds to the so-called collective behavior of the FC,[1] which is characterized by the concentration of magnetic grains larger than some critical value, depending on sample dimensions. Lower concentrations of the magnetic grains leads to the local distortions of the director nearby every particle independently of the others.

In this paper we study orientational and magnetic properties of the FC in the magnetic field which is perpendicular to the spiral axis. As it is well-known, the increasing of the magnetic field strength **H** in pure CLC with positive diamagnetic anisotropy χ_a leads to the increasing of the cholesteric pitch and if H reaches the critical value $H_c = (\pi q_0/2)\sqrt{K_{22}/\chi_a}$ (q_0 is the wave number of the spiral in the zero field, K_{22} is the twist modules), the spiral pitch diverges and cholesteric-nematic transition takes place. The typical value of H_c is about $10^4 Oe$ for pure CLC. However, in FC there is one more (dipolar) mechanism of the magnetic field influence on the spiral pitch. For this reason we may expect that the critical value H_c will be lower than in pure CLC.

2. FREE ENERGY OF THE FERROCHOLESTERIC

The free energy density of the FC is

$$F = F_1 + F_2 + F_3 + F_4,$$

$$F_1 = \frac{1}{2}[K_{11}(\text{div}\,\mathbf{n})^2 + K_{22}(\mathbf{n}\,\text{rot}\,\mathbf{n} + q_0)^2 + K_{33}(\mathbf{n}\times\text{rot}\,\mathbf{n})^2],$$

$$F_2 = -M_s f\mathbf{m}\mathbf{H}, \tag{1}$$

$$F_3 = -\frac{1}{2}\chi_a(\mathbf{n}\mathbf{H})^2,$$

$$F_4 = \frac{fk_BT}{v}\ln f.$$

Here K_{11}, K_{22} and K_{33} are the splay, twist and bend elastic constants of the CLC, respectively; M_s being the saturation magnetization of the ferromagnetic grain, f is the volume fraction of the particles in the suspension, v is the particle volume, k_B is the Boltzmann constant, T is the temperature, **m** is a unit vector along the particle axis. The first term in Equation (1) represents the free energy density of the orientation-elastic deformation of the director (Frank potential). The terms F_2 and F_3 describe the dipolar and the quadrupolar mechanisms of the interaction of the particle magnetic moments $\boldsymbol{\mu} = M_s v\mathbf{m}$ and the diamagnetic CLC matrix with the magnetic field **H**, respectively. The last term in Equation (1) gives the contribution of the mixing entropy of the ideal magnetic particles solution. The volume fraction of the magnetic admixture is assumed to be sufficiently low ($f \ll 1$) and the interparticle magnetic dipole-dipole interaction is negligible. We assume also the strong anchoring between the CLC molecules and the surface of the magnetic grains to provide the close connection between the orientations of the main particle axes **m** and the CLC director **n**.

In the zero field the magnetic grains are uniformly distributed over the FC sample

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volume $V(f = f_0 = Nv/V)$ and their magnetic moments $\boldsymbol{\mu}$ rotate with the director $\mathbf{n} = \mathbf{n}_0 = (\cos q_0 z, \sin q_0 z, 0)$, so that $\mathbf{m} \| \mathbf{n}$ if the planar conditions on the particle surfaces take place or $\mathbf{m} \perp \mathbf{n}$ if there are homeotropic conditions, and the FC spiral is forming with the pitch $p_0 = 2\pi/q_0$. Let us direct the external magnetic field $\mathbf{H} = (0, H, 0)$ normal to the spiral axis of the FC and assume that the anisotropy χ_a of the CLC matrix is positive. Magnetic field distorts the helicoidal structure of the FC spiral and the dependence of the director components on the coordinate z becomes non-harmonical

$$\mathbf{n} = (\cos \phi(z), \sin \phi(z), 0) \tag{2}$$

The expression (1) for the free energy density takes the following form after the inserting of the Equation (2):

$$F = \frac{K_{22}}{2}\left(\frac{d\phi}{dz} - q_0\right)^2 - \frac{\chi_a H^2}{2}\sin^2\phi - M_s f H \sin\phi + \frac{f k_B T}{v}\ln f. \tag{3}$$

We assume that planar conditions ($\mathbf{m} \| \mathbf{n}$) take place here and below. Let us use as the units of length q_0^{-1} and as magnetic field strength $H_0 = M_s f_0/\chi_a$. This choice of units leads to the value of the unperturbed pitch is equal to 2π. The choice of H_0 is stipulated by following circumstance. The diamagnetic (F_3) and the ferromagnetic (F_2) contributions into the free energy density and therefore the spontaneous and induced magnetization are the same order at $H \sim H_0$. This choice of units allows to rewrite the Equation (3) in the dimensionless variables:

$$\frac{F}{K_{22}q_0^2} = \frac{1}{2}\left(\frac{d\phi}{dz} - 1\right)^2 - \frac{R\sigma^2}{2}\sin^2\phi - \frac{R\sigma f}{f_0}\sin\phi + \frac{\kappa f}{f_0}\ln f, \tag{4}$$

where the following identifications are chosen:

$$\sigma = \frac{H}{H_0}, \quad R = \frac{\chi_a H_0^2}{K_{22}q_0^2}, \quad \kappa = \frac{f_0 k_B T}{v K_{22} q_0^2} = (\lambda q_0)^{-2}. \tag{5}$$

The parameter R characterizes the regimes of the spiral untwisting: if $R >> 1$ the spiral untwisting is realized due to dipolar (ferromagnetic) mechanism and if $R << 1$—due to quadrupolar (diamagnetic) one. The parameter κ is connected with the square ratio of two characteristic lengths λ and q_0^{-1}, where λ is a scale of the region where the concentrational statification takes place.

3. THE BASIC EQUATIONS

The volume density of the total free energy of FC

$$\bar{F} = V^{-1}\int F\, dV \tag{6}$$

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is the functional in respect to functions $\phi(z)$ and $f(z)$. Minimization F over $f(z)$ under the condition of the constancy of the magnetic particles number

$$\int f\,dV = N\nu$$

leads to the concentration distribution

$$f = f_0 Q \exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\}, \tag{7}$$

$$Q^{-1} = p^{-1}\int_0^p \exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\}dz. \tag{8}$$

Equation (7) describes the so-called segregation effect[1]: magnetic field **H** induces the redistribution of the magnetic admixture in the FC and so the concentration of the magnetic particles increases in those parts of a sample where the director **n** and the field **H** are parallel.

Minimization Equation (6) over $\phi(z)$ gives rise to the equation

$$\frac{d^2\phi}{dz^2} + \frac{R\sigma f}{f_0}\cos\phi + R\sigma^2\sin\phi\cos\phi = 0.$$

One can find its first integral using the relation (7) and obtains

$$\left(\frac{d\phi}{dz}\right)^2 + 2\kappa Q\exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\} + R\sigma^2\sin^2\phi = C, \tag{9}$$

where C is an integration constant. Equation (9) enables one to determine the dependence $\phi(z)$:

$$z = \int_0^\phi \frac{d\phi}{\sqrt{A}}, \tag{10}$$

$$A = C - 2\kappa Q\exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\} - R\sigma^2\sin^2\phi. \tag{11}$$

The spiral pitch of FC in the presence of the magnetic field **H** corresponds to a variation $\Delta\phi = 2\pi$, so using Equation (10), we find

$$p = \int_0^{2\pi}\frac{d\phi}{\sqrt{A}}. \tag{12}$$

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We determine C by minimization of the free energy (6). After the integration with the help of Equation (9), we obtain

$$\frac{\tilde{F}}{K_{22}q_0^2} = p^{-1}\int_0^{2\pi} d\phi\sqrt{A} - 2\pi p^{-1} + \frac{1-C}{2} + \kappa\ln(ef_0Q). \tag{13}$$

Minimizing this expression over C, we obtain the equation for C:

$$\int_0^{2\pi} d\phi\sqrt{A} = 2\pi. \tag{14}$$

For the purpose of further consideration it is useful to change the integration variable in Equation (8). Using Equations (9) and (10), one obtains the following equation for Q:

$$\int_0^{2\pi}\left[1 - Q\exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\}\right]A^{-1/2}\,d\phi = 0. \tag{15}$$

In order to calculate magnetic characteristics of the FC we remind that if strong anchoring between the orientations of the magnetic particles and CLC matrix takes place ($\mathbf{m}\|\mathbf{n}$) then the magnetization per unit volume of the FC is parallel to the local director $\mathbf{M} = M_s f\mathbf{n}$. Taking into account Equations (2) and (7), we obtain the following equation for the reduced magnetization $\mathbf{M} = \mathbf{M}/M_s f_0$ which is the combination of the orientation $\phi(z)$ and concentrational $f(z)$ distributions:

$$\mathbf{M} = Q\mathbf{n}\exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\}. \tag{16}$$

This expression enables one to determine average over the pitch of the spiral components of the reduced magnetization:

$$\langle\mathbf{M}\rangle = p^{-1}\int_0^p \mathbf{M}\,dz$$

Changing the integration variable with the help of Equation (9) one obtains

$$\begin{aligned}\langle M_x\rangle &= \langle M_z\rangle = 0,\\ \langle M_y\rangle &= p^{-1}Q\int_0^{2\pi} A^{-1/2}\sin\phi\exp\left\{\frac{R\sigma}{\kappa}\sin\phi\right\}d\phi.\end{aligned} \tag{17}$$

Thus, the total system of equations, which enables to determine the orientational and magnetic characteristics of the FC consists from Equations (2), (7), (10), (12), (14)–(17).

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4. THE CRITICAL FIELD

The system of orientational and magnetic state equations of the FC, that has been obtained in the previous section, makes it possible to study the magnetic field influence on the orientational structure and magnetic properties of the FC.

The field **H**, being taken in the direction normal to the FC spiral, causes the untwisting of the spiral structure if the field strength reaches the critical value. However, there is no necessity to solve numerically the system of equations in order to calculate critical field strength. It can be obtained[2] using the condition such as the equality between the values of the free energy for a magnetically oriented system (see Equations (13), (14))

$$\frac{\tilde{F}}{K_{22}q_0^2} = \frac{1 - C}{2} + \kappa \ln(ef_0Q) \tag{18}$$

and for an untwisting ferronematic sample

$$\frac{F}{K_{22}q_0^2} = \frac{1}{2} - R\sigma \sin\phi_0 + \kappa \ln f_0 - \frac{R\sigma^2}{2}\sin^2\phi_0. \tag{19}$$

Here ϕ_0 is an angle of the director orientation which does not depend on coordinates. The value of ϕ_0 can be readily found by minimizing the free energy (19) and being equal $\pi/2$, i.e. the ferronematic director is oriented along the magnetic field.

The equality of the two expressions (Equations (18) and (19)) for $\phi_0 = \pi/2$ and for the critical value of the quantity Q being equal to $Q_c = \exp\{-R\sigma_c/\kappa\}$, leads to the value $C_c = 2\kappa + R\sigma_c^2$. Here σ_c is the critical reduced magnetic field strength.

It can be verified easily that substitution the above mentioned values Q_c and C_c into Equation (12) gives rise to the pitch of the spiral tends to infinity: $p \to \infty$. Inserting Q_c and C_c into Equation (14) one finds the following equation

$$\int_0^{\pi/2} d\phi\sqrt{B} = \pi/2,$$
$$B = 2\kappa\left\{1 - \exp\left[\frac{R\sigma_c}{\kappa}(\sin\phi - 1)\right]\right\} + R\sigma_c^2\cos^2\phi. \tag{20}$$

This equation determines the dependence of the critical field value σ_c on the FC material parameters R and κ.

For small values of σ_c the critical behavior can be attained in the case $R \gg 1$ and $\sigma_c = \pi^2/16R$, as can be easily seen from Equation (20). So in this case the dipolar (ferromagnetic) mechanism of the spiral untwisting is realized. The above mentioned value σ_c corresponds to

$$H_c = \frac{\pi^2}{16}\frac{K_{22}q_0^2}{M_sf_0}$$

and coincides with the result,[1] where the quadrupolar interaction between the magnetic field and liquid-crystalline matrix does not take into account.

For $R \ll 1$ the diamagnetic (quadrupolar) mechanism of the spiral untwisting occurs for high fields $\sigma_c = (\pi^2/4R)^{1/2}$, i.e. $H_c = (\pi q_0/2)\sqrt{K_{22}/\chi_a}$ as in pure CLC.[3]

Figure 1 shows the dependence $\sigma_c(R)$ for some values of κ. This dependence has been received by numerical simulation of Equation (20). The dashed lines

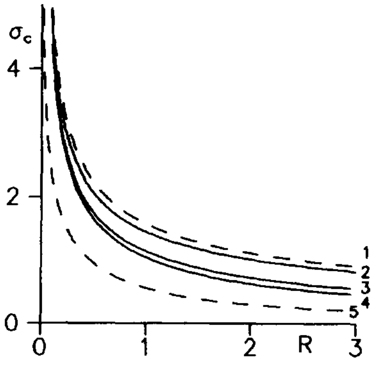

FIGURE 1 Critical magnetic field strength vs parameter R. Curve 1—$\kappa = 0$, 2—$\kappa = 0.1$, 3—$\kappa = 1$, 4—$\kappa = 10$, 5—$\kappa = \infty$.

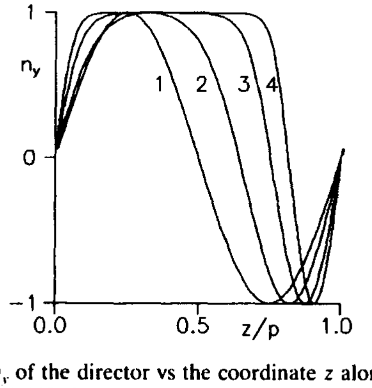

FIGURE 2 The component n_y of the director vs the coordinate z along the spiral for $R = 100$, $\kappa = 0.5$. Curve 1—$\sigma = 0$, 2—$\sigma = 0.005$, 3—$\sigma = 0.01$, 4—$\sigma = 0.015$.

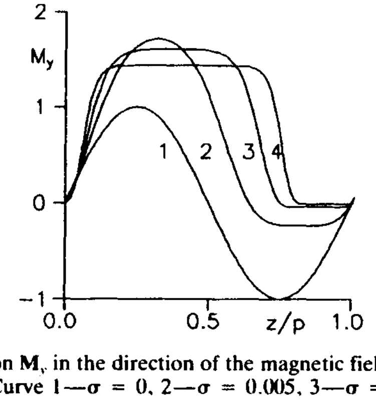

FIGURE 3 The magnetization M_y in the direction of the magnetic field vs the coordinate z along the spiral for $R = 100$, $\kappa = 0.5$. Curve 1—$\sigma = 0$, 2—$\sigma = 0.005$, 3—$\sigma = 0.01$, 4—$\sigma = 0.015$.

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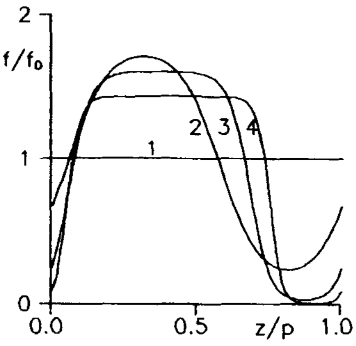

FIGURE 4 The concentration of the magnetic particles vs the coordinate z along the spiral for R = 100, κ = 0.5. Curve 1—σ = 0, 2—σ = 0.005, 3—σ = 0.01, 4—σ = 0.015.

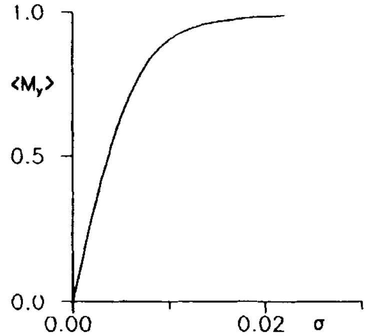

FIGURE 5 The average magnetization of the FC vs magnetic field strength for R = 100, κ = 0.5.

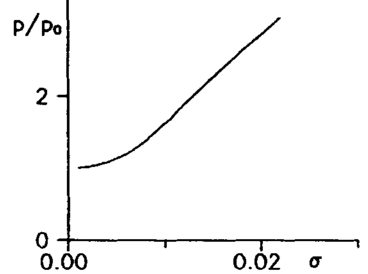

FIGURE 6 The pitch of the FC spiral vs magnetic field strength for R = 100, κ = 0.5.

correspond to the limiting cases $\kappa \to 0$ and $\kappa \to \infty$. For $\kappa \to 0$ the concentrational redistribution is unessential and it is verified easily that $\sigma_c = \pi/2\sqrt{R}$ as in pure CLC. For $\kappa \to \infty$ the dependence $\sigma_c(R)$ may be written in parametrized form

$$R = \pi^2 \frac{2}{(2\alpha + sh2\alpha)^2}, \quad \sigma_c = sh\alpha.$$

In this case the length of segregation λ is much more than the unperturbed pitch

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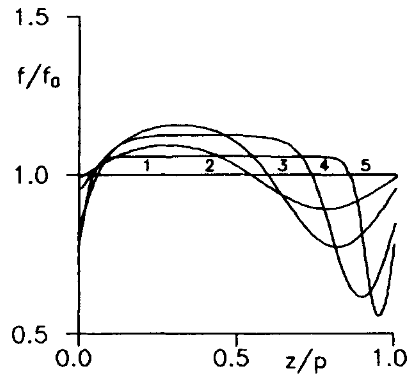

FIGURE 7 The concentration of the magnetic particles vs the coordinate z along the spiral for $R = \kappa = 2$. Curve 1—$\sigma = 0$, 2—$\sigma = 0.1$, 3—$\sigma = 0.1$, 4—$\sigma = 0.3$, 5—$\sigma = 0.32$.

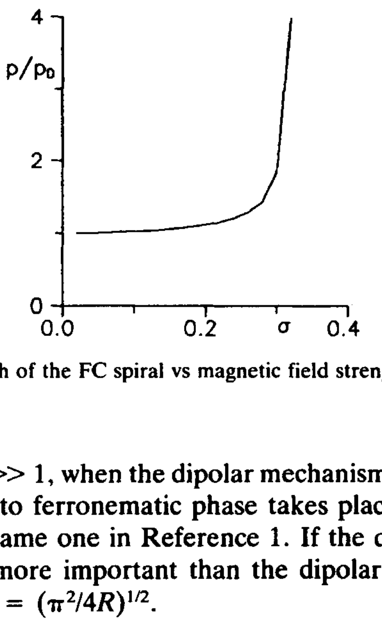

FIGURE 8 The pitch of the FC spiral vs magnetic field strength for $R = \kappa = 2$.

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p_0 of the spiral and for $R >> 1$, when the dipolar mechanism of the spiral untwisting prevails, the transition into ferronematic phase takes place if $\sigma_c = \pi^2/16R$. This result is identical to the same one in Reference 1. If the quadrupolar mechanism of the field influence is more important than the dipolar one, i.e. $R << 1$, the critical value becomes $\sigma_c = (\pi^2/4R)^{1/2}$.

As it is seen from Figure 1 if the regime of the spiral untwisting changes from quadrupolar ($R << 1$) to dipolar ($R >> 1$) one, the critical value σ_c of the ferrocholesteric-ferronematic transition field strength decreases.

5. LOW FIELDS

For low fields ($\sigma << 1$) the system of the orientational and magnetic state equations can be easily solved. In the second order of power series expansion in σ one obtains

$$z = \phi\left(1 + \frac{R^2\sigma^2}{2}\right) + 2R\sigma\sin^2\frac{\phi}{2} - \frac{\sigma^2}{8}\left(\frac{R^2}{\kappa} + R + 3R^2\right)\sin 2\phi,$$

$$\frac{f}{f_0} = 1 + \frac{R\sigma}{\kappa}\sin\phi + \frac{R^2\sigma^2}{4\kappa^2}[2\sin^2\sigma - (1 + 2\kappa)],$$

$$\frac{p}{p_0} = 1 + \frac{R^2\sigma^2}{2}, \tag{21}$$

$$\mathbf{M} = \frac{f}{f_0}\mathbf{n},$$

$$\langle M_y\rangle = \frac{R\sigma}{2\kappa}(1 + \kappa).$$

These results show, that even low magnetic field induces the redistribution of the magnetic admixture along the period of the spiral structure, and the concentration of the solid phase increases in the **H** direction, i.e. in the direction corresponds to $\phi = \pi/2$. The variation of the spiral pitch p is proportional to H^2 instead of H^4 in pure CLC. Such strong influence of the magnetic field on the FC pitch is connected with the interaction between the field and the magnetic moments of the particles in the first turn, whereas the cholesteric matrix has low sensitivity to the weak field.

The redistribution of the magnetic admixture in FC leads to the magnetization of the sample in the field direction: $\langle M_y\rangle \neq 0$. The initial susceptibility χ of the FC is given by

$$\chi = \chi_a\frac{R(1 + \kappa)}{2\kappa} \tag{22}$$

and for typical values of material parameters $M_s \sim 10^3 G$, $f_0 \sim 10^{-5}$, $\nu \sim 10^{-15}$ cm^{-3} and $T \sim 300$ K, its value is about four or five orders of magnitude higher than the diamagnetic susceptibility χ_a for pure CLC.

6. RESULTS

Figures 2–4 show the results of the numerical simulations of the orientational and magnetic equations of state of FC for $R = 100$ and $\kappa = 0.5$ and some values of magnetic field strength σ. Curves 1 correspond to $\sigma = 0$ and the spiral structure of the director has the helicoidal character. Because of the strong anchoring between the particles and the director, the magnetization vector **M** spirals in phase with the director (see Figure 3, curve 1) and the concentration of the solid phase is constant ($f = f_0$) along the spiral. If magnetic field is applied (curves 2, $\sigma = 0.005 \leq \sigma_c$

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= 0.078), it deforms the director field (Figure 2) and the magnetization (Figure 3), and induces the redistribution of the magnetic admixture (Figure 4). The external magnetic field increasing leads to the segregation effect: the particles accumulate in those parts of the spiral where the director is parallel to the field, and the appearance of the so-called depleation layers, where the particle concentration is strongly reduced. As a result of such redistribution of the magnetic admixture, FC magnetizes in the field direction: $\langle M_y \rangle \neq 0$ if $\sigma \neq 0$ (see Figure 5). The average magnetization $\langle M_y \rangle$ increases with σ increasing, and tends to saturation if $\sigma \rightarrow \sigma_c$. The pitch of spiral structure increases with σ (see Figure 6) and tends to infinity for $\sigma \rightarrow \sigma_c$. Then σ is close to σ_c, the region of favourable orientation for **n** and **H** spreads all over the greater part of spiral, the concentrational distribution (Figure 4) tends to stepped kind, and $f \rightarrow f_0$ at the point of transition to the ferronematic phase and the magnetic grains will be uniformly distributed over the sample.

It should be noted that relatively weak fields (the above mentioned values R = 100 and κ = 0.5 correspond to σ_c = 0.078) used in our numerical simulations (Figures 2–6) give rise to the essential changes in the orientational and magnetic state of FC.

Variation of the FC material parameters does not change qualitatively the profiles of the director, magnetization and concentration—see Figures 7 and 8, where dependencies $f(z)$ and $p(\sigma)$ are shown for $R = \kappa = 2$.

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