Stratification of ferroparticles caused by gravitational and magnetic fields in soft ferronematics

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Abstract. In the framework of continuum theory we study the magnetic particles stratification caused by gravitational and magnetic fields in ferronematic, i.e., a highly dispersed suspension of ferroparticles in a nematic liquid crystal. We consider the so-called soft ferronematic, where the coupling energy between the liquid crystal and the particle surfaces is finite, which allows to consider the director and magnetization of the ferronematic as independent variables. We show how under the influence of an external uniform magnetic field due to the segregation effect heavy impurity ferromagnetic particles begin to float up in a lower-density fluid, moving opposite to the gravity field. As an example, several types of suspensions with material parameters corresponding to actually synthesized ferronematics with different ratios between the two competing mechanisms of separation of impurity particles (segregation and gravity) are considered.

1. Introduction
Ferronematic (FN) is the name for colloidal suspension of anisometric ferromagnetic particles in nematic liquid crystal (NLC) [1, 2]. The unusual physical properties of FNs, unlike pure liquid crystals (LCs), associate with two different orientational mechanisms in an applied magnetic field. The first of these is typical for LCs and is due to the anisotropy of the diamagnetic susceptibility of the LC matrix (the quadrupole mechanism). Another mechanism occurs only in the system, which has dispersed ferromagnetic particles (the dipole mechanism). Under the influence of the magnetic field, the ferroparticles change their orientation, and the coupling forces between LC molecules and the surface of ferroparticles transfer the created mechanical rotation to the LC matrix. In this way, two orientational mechanisms generate numerous new effects in LC magnetic suspensions that are not only of interest to basic materials science, but also remain attractive in terms of its application.

Usually, experiments use cells with a thickness not exceeding 100 μm, where the distribution of particles over the layer thickness can most often be considered uniform. However, with a greater cell thickness, the impurity may have a significant vertical concentration gradient caused by a gravitational field. As a result, in the absence of an external magnetic field, the ferroparticles accumulate near the lower boundary of the vertical layer of the FN. This phenomenon is known as gravitational stratification or sedimentation. Under the influence of a magnetic field ferroparticles accumulate in those areas of the layer where the sum of their magnetic energy in the magnetic field and orientational
energy in the LC matrix is minimal. This phenomenon is specific for FNs and is called the segregation effect [1].

The present paper deals with theoretical study of the ferroparticles concentration stratification in the twist cell of the FN caused by the gravitational and magnetic fields. We take into account the finite energy of coupling between the LC molecules and impurity particles (soft FN), where the LC director and magnetization are independent variables; a rigid coupling is studied in [3]. We also take into account the interaction of the LC matrix with an external magnetic field, which has not been done before either. We study two samples of FNs with different ratios between two competing mechanisms of particles stratification, i.e., between gravity sedimentation and separation caused by the segregation effect.

2. The continuum description

We consider FN in a twist planar cell of thickness $L$. The $x$ axis of the coordinate system is directed parallel to the bounding plates, whereas the $z$ axis is perpendicular to them; the origin of coordinates is on the lower boundary of the layer. We assume that the coupling between the director and the layer boundaries is absolutely rigid and planar, i.e., the director is fixed at the boundaries and its direction coincides with the easy orientation axis $e=(e_0,0,0)$ for $z=0$ and $l=(0,l,0)$ for $z=L$. We also consider the soft planar coupling of the LC matrix and ferroparticles [4], so that in the absence of a magnetic field the alignment of the director and long axes of particles coincides. Let us direct the magnetic field $H=(0,H,0)$ in parallel to the boundaries of the layer along the $y$ axis. We direct the gravitational acceleration $a=(0,0,-a)$ antiparallel to the axis $z$. Schematic representations of the FN in a twist planar cell is shown in figure 1.

Figure 1. Twist planar cell of FN in the gravitational and magnetic fields. The choice of coordinate system.

The resulting distortion of the FN orientational structure in equilibrium generated in the fields corresponds to the minimum of free energy [3–5]
where $K_{11}$, $K_{22}$, $K_{33}$ are the Frank elastic moduli; $n$ is the LC director; $\chi_{\alpha} > 0$ is the anisotropy of LC diamagnetic susceptibility, which is positive therefore, the director tends to rotate in the magnetic field direction; $f$ is the local volume fraction of magnetic particles in the suspension with magnetic moments $\mu = M_s \mathbf{m}$ aligned parallel to the local director $n$ in the absence of the magnetic field; $\mathbf{m}$ is the unit vector of suspension magnetization; $M_s$ is the saturation magnetization of the particle substance; $v$ is the ferroparticle volume; $k_B$ is the Boltzmann constant; $T$ is the temperature; $\rho_p$ and $\rho_{LC}$ are the mass densities of particles and LC, respectively; $a$ is gravitational acceleration module; $W > 0$ is the density of surface energy of interaction between the particles and the LC matrix (we assume this value is positive, so that in the absence of the external magnetic field the minimum of free energy corresponds to parallel orientation of the director and magnetization $n \parallel m$, i.e., planar coupling conditions of LC with magnetic particles); $d$ is the transverse diameter of a particle. In the diluted suspension the average volume fraction of ferroparticles is low $\bar{f} = N_\nu/N << 1$ (here $N$ is the number of magnetic particles in the suspension, $V$ is the FN volume) that allows us to neglect interparticle magnetic dipole-dipole interactions.

In the considered geometry (see figures 1 and 2) the deformation of the director and magnetization can be presented in the form

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

where $\varphi(z)$ and $\psi(z)$ are the angles of the director and magnetization deviations from the $x$ axis, respectively. Let us choose the layer thickness $L$ as the unit of length and define the following dimensionless quantities: coordinate $\zeta = z/L$, field strength $h = HL\sqrt{\chi_{\alpha}/K_{22}}$, reduced volume fraction $g = f/\bar{f}$. We also introduce the dimensionless parameters [5]

$$
b = \frac{M_s \bar{f} L}{\sqrt{K_{22} \chi_{\alpha}}}, \quad \sigma = \frac{W \bar{f} L^2}{K_{22} d}, \quad \kappa = \frac{k_B T \bar{f} L^2}{K_{22} v}, \quad \alpha = \frac{a \bar{f} L^3}{K_{22}} (\rho_p - \rho_{LC}).
$$

The parameter $b$ characterizes the relative action of quadrupole and dipolar mechanisms on the orientational and magnetic structure of FN; at $b > 1$ orientational distortions arise mainly due to the dipole mechanism, and in the case $b < 1$ they are caused by the quadrupole mechanism. The parameter $\sigma$ represents the dimensionless energy of coupling between the ferroparticles and the LC matrix. The segregation parameter $\kappa$ is the squared ratio $\kappa = (L/\lambda)^2$ of two characteristics length, viz. the layer thickness $L$ and segregation length $\lambda = [K_{22} v/(k_B T \bar{f})]^{1/2}$, which specifies the characteristic scale of the region of concentration redistribution of the ferroparticles (the so-called segregation effect [1]). If the characteristic scale of the concentration stratification area $\lambda$ is much less than $L$ then the parameter $\kappa >> 1$ and the segregation effects are weak and they can be neglected, while for $\kappa \approx 1$ nonuniform distribution of the magnetic particles becomes noticeable. The last parameter $\alpha$ determines the intensity of gravitational sedimentation of the impurity particles. For $\alpha << 1$ the spatial distribution of dispersed particles is slightly different from the uniform distribution.
3. The equations of equilibrium state

The equilibrium state of the FN corresponds to the minimum of free energy (1), minimization of which over \( \phi(\zeta) \), \( \psi(\zeta) \) and \( g(\zeta) \) yields the following system of equations

\[
\frac{\partial^2 \phi}{\partial \zeta^2} + \frac{1}{2} h^2 \sin 2 \phi - \sigma g \sin 2(\phi - \psi) = 0, \\
\]

\[
b h \cos \psi + \sigma \sin 2(\phi - \psi) = 0, \\
\]

\[
g(\zeta) = Q \exp \left\{ \frac{b h \sin \psi + \sigma}{\kappa} \cos^2 (\phi - \psi) - \frac{\alpha}{\kappa} \zeta \right\}.
\]

Here normalization constant \( Q \) can be found with the condition of constancy of the magnetic particles number \( N \) in a suspension

\[
Q^{-1} = \int_{0}^{1} \exp \left\{ \frac{b h \sin \psi + \sigma}{\kappa} \cos^2 (\phi - \psi) - \frac{\alpha}{\kappa} \zeta \right\} d\zeta.
\]

The system of equations (4) – (7) with the boundary conditions

\[
\phi(0) = 0 \quad \text{and} \quad \phi(1) = \pi / 2
\]

form a closed boundary value problem for determining the orientation and concentration profiles \( \phi(\zeta) \), \( \psi(\zeta) \) and \( g(\zeta) \) of the FN in the magnetic and gravitational fields.

4. The calculation results

4.1. Weak stratification of particles

Let us estimate dimensionless parameters for the first sample of FN according to [6] (in CGS units) \( K_{22} = 3.5 \times 10^{-7} \) dyne, \( \chi_0 = 1.3 \times 10^{-7} \), \( M_s = 170 \) Gs, \( d = 7 \times 10^{-6} \) cm, \( v = 1.9 \times 10^{-17} \) cm\(^3\), \( \rho_p = 5.6 \) g/cm\(^3\), \( \rho_{LC} = 1 \) g/cm\(^3\), \( T = 300 \) K, \( W \approx 3 \times 10^{-3} \) dyne/cm, assuming the average volume fraction of ferroparticles \( \bar{f} = 5 \times 10^{-6} \) and the layer thickness \( L = 2.5 \times 10^{-2} \) cm, we obtain \( b \approx 100 \), \( \sigma \approx 4 \), \( \kappa \approx 20 \) (weak segregation effect) and \( \alpha \approx 1 \). Dimensionless magnetic field \( h \) becomes of the order of unity for \( H \approx 66 \) Oe. Here we have to define another important dimensionless parameter \( \zeta_* = \kappa / \alpha \), which is characteristic scale of the gravitational stratification measuring in the units of the layer thickness [3]. The equilibrium distribution of the concentration of impurity particles over the layer thickness in zero magnetic field can be considered approximately uniform only for \( \zeta_* >> 1 \). For the parameters estimated above \( \zeta_* = 20 \) and we should expect weak gravitational separation of the impurity particles in such FN sample.

The results of numerical solution of equations. (4) – (7) for \( b = 100 \), \( \sigma = 4 \), \( \kappa = 20 \) and \( \alpha = 1 \) are presented in figures 3.
Figure 3. Spatial distributions of the orientation angles of the LC director (a), magnetization (b) and the reduced volume fraction of ferroparticles (c) for different values of the magnetic field strength $h$. The case of weak stratification. Estimations of dimensionless parameters were obtained according to [6].

In the absence of a magnetic field the director and magnetization distributions have solution

$$\phi(\zeta) = \psi(\zeta) = \frac{\pi\zeta}{2}$$  \hspace{1cm} (9)

and the concentration distribution of ferroparticles is described by the formula

$$g(\zeta) = \frac{\kappa}{\alpha} \left[ 1 - \exp\left( -\frac{\alpha}{\kappa} \right) \right]^{-1} \exp\left( -\frac{\alpha\zeta}{\kappa} \right)$$  \hspace{1cm} (10)

(the dashed lines in figures 3), as seen from it, the maximum concentration is at the lower boundary of the layer $\zeta = 0$ due to gravitational sedimentation.

In our case the FN is soft [4], i.e., there is finite coupling energy between the LC and the particle surfaces. This means that the LC director at the surface of ferroparticles might deviate from the most energetically favorable direction at the expense of some quite moderate portion of energy conveyed to the particle by the applied magnetic field. Under the magnetic field action the magnetization gets separated from the director, ferroparticles tend to reorient in the field direction and for $h > 1$ the orientation angle of magnetization is $\psi(\zeta) \approx \pi/2$ in the whole FN layer (see figure 3b). Due to small value of anisotropy of LC diamagnetic susceptibility $\chi_a \sim 10^{-7}$, sufficiently large magnetic fields are required to reorient the LC molecules in the direction of the field. Only for sufficiently large magnetic fields $h > 1$ the LC molecules orient in the direction of the field (see figure 3a).

As the energy function of the particle includes Zeeman contribution along with the orientational and the gravity potentials (see terms in equation (6), respectively), the situation is that for a particle the decrement of the surface orientation energy is greater than the increment of its gravitational energy associated with its vertical ascend in the FN cell. The magnetic field that strives to align the particle magnetic moment along itself is an intermediary in this process. This effect produces a substantial anti-gravitational stratification of the particles and the non-monotonic dependence of the particles on the vertical dimensionless $\zeta$ coordinate (see figure 3c). When the magnetic field is switched on, a lifting force appears that acts on the particles opposite to the force of gravity. As can be seen from figure 3c (curves $h = 0.01$, $h = 0.1$ and $h = 1$) the impurity begins to accumulate at the upper boundary of the layer. In large magnetic fields ($h > 1$) the directions of the LC director and the magnetization begin to coincide, with the exception of a narrow region near the lower boundary of the
layer (see figures 3a and 3b), which causes reverse migration of ferroparticles towards the lower boundary of the FN layer (see figure 3c).

As it is seen from figure 3c, the distribution of ferroparticles over the layer thickness \(g(\zeta)\) varies slightly and lies in the range of 0.85 to 1.05 for the presented values of the magnetic field strength \(h\).

4.2. Strong stratification of particles
Let us estimate dimensionless parameters for the second sample of FN according to [7–9]

\[
K_{22} = 3.7 \times 10^{-7} \text{dyne}, \quad \chi_a = 3.5 \times 10^{-8}, \quad M_s \approx 10 \text{ Gs}, \quad d = 8 \times 10^{-6} \text{cm}, \quad v = 6 \times 10^{-15} \text{cm}^3, \quad \rho_p = 5 \text{g/cm}^3, \quad \rho_{LC} = 1 \text{g/cm}^3, \quad T = 300 \text{K}, \quad W = 1.2 \times 10^{-3} \text{dyne/cm},
\]

assuming the average volume fraction of ferroparticles \(\bar{f} = 10^{-4}\) and the layer thickness \(L = 10^{-2} \text{cm}\), we obtain \(b \approx 100, \quad \sigma \approx 4, \quad \kappa \approx 0.2\) (strong segregation effect) and \(\alpha \approx 1\). The unit dimensionless field \(h_{1} = 1\) corresponds to \(H \approx 325 \text{Oe}\). For the gravitational stratification length we obtain \(\zeta_s = 0.2\) and we should expect strong gravitational separation of the impurity particles.

The results of numerical solution of equations (4) – (7) for \(b = 100, \quad \sigma = 4, \quad \kappa = 0.2\) and \(\alpha = 1\) are presented in figure 4. Even in zero magnetic field, the impurity distribution over the layer thickness is highly non-uniform (dashed curve in figure 4).

**Figure 4.** Spatial distributions of the orientation angles of the LC director (a), magnetization (b) and the reduced volume fraction of ferroparticles (c) for different values of the magnetic field strength \(h\). The case of strong stratification. Estimations of dimensionless parameters were obtained according to [7–9].

In the presence of magnetic field, the orientational distributions of LC molecules and ferroparticles, which are shown in figures 4a and 4b, respectively, only slightly differ from the case of weak segregation, which is presented in figures 3a and 3b. Under the influence of the magnetic field the initial distribution of ferroparticles significantly changes and the impurity floats up to the upper layer boundary. Even at \(h = 0.1\) the lower half of the layer becomes free from the particles and corresponds to pure NLC. In this case, the distribution of the LC director is as non-uniform as possible, and strong segregation effects significantly dominate over the gravitational ones. With the magnetic field strength increasing, when the LC director is oriented along the field, not only near the upper boundary of the layer, but also in its middle (see figure 4a, curve \(h = 5\)), particles migrate towards the lower boundary of the layer, and the concentration maximum approximately corresponds to the middle of the layer.

In large fields the LC director is predominantly oriented in the direction of the field in the whole layer. The only exception is a narrow area near the lower boundary, where due to rigid coupling between director and boundary plate, LC molecules are not able to turn in the field direction (figures 4a, curve \(h = 50\)). For such an almost uniform spatial distribution of the director, the segregation
effect becomes insignificant and gravitational stratification begins to dominate in the system and thus the distribution of ferroparticles becomes close to initial state at \( h = 0 \).

5. Summary
In the present paper, we have studied two competing separating mechanisms of magnetic particles in the soft FN. On the one hand, under the influence of gravitational field, particles tend to be accumulated near the lower boundary of the layer, and on the other hand, due to the effect of segregation, a concentration gradient opposed to gravity appears in an external uniform magnetic field. As a result, particles begin to accumulate in the upper part of the layer. In the case of strong segregation, the lower part of the FN layer becomes free from the particles.

In addition, for the soft FN with finite coupling of the impurity particles and LC molecules, the magnetization gets separated from the LC director and ferroparticles are oriented along the magnetic field while the director’s orientation remains almost unchanged.

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