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Adsorption Phenomena and Macroscopic Properties of Ferronematics Caused by Orientational Interactions

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ADSORPTION PHENOMENA AND MACROSCOPIC PROPERTIES OF FERRONEMATICS CAUSED BY ORIENTATIONAL INTERACTIONS

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We have studied the effect of adsorption and desorption of rod-like magnetic grains on the macroscopic properties of ferronematics in a ferronematic cell. An external magnetic field controls the equilibrium between ferroparticles in the bulk and those adsorbed on the cell surfaces. The magnetic field can thus influence the anchoring and the nematic orientational texture. In the presence of ferroparticle adsorption, the segregation effect is diminished, and the system becomes less susceptible to bulk ferroparticle coagulation.

Keywords: adsorption; ferroparticle; liquid crystal; magnetic field

INTRODUCTION

Ferronematics (FN's) are highly dispersed colloidal suspensions of ferrite grains, in which the suspending medium is a nematic liquid crystal (NLC). These systems were first proposed on theoretical grounds

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by Brochard and de Gennes [1]. They were first synthesized by Chen and Amer [2] using a thermotropic MBBA NLC matrix and γ-Fe_2O_3 rod-like grains coated with DMOAP, which provides homeotropic anchoring on their surfaces.

One main feature of these materials is their intrinsic high magnetic susceptibility. This occurs because the nematic molecules stick to the ferroparticle surfaces, causing macroscopic collective behavior of the ferrite grains [2–6]. Collective particle behaviour occurs when the orientational coupling between the magnetic and LC components in the FN is sufficiently strong. This sets in at volume particle fraction $f \geq f^* \sim Kd/(2W_pD^2)$[3], where K is the mean value of the nematic elastic constants, d is the diameter of a rod-like particle, D is the FN cell thickness, and W_p is the homeotropic anchoring energy at the ferroparticle surfaces. Magnetic-field-induced ferroparticle rotations are transmitted to the entire NLC matrix. This changes the optical properties of the matrix, partially as regards birefringence. The magnetic Frederiks transition in ferronematics is threshold-free and already occurs in weak external magnetic fields. Ultra-fine ferroparticles enable the FN to be particularly sensitive to magnetic fields [6]. These properties are the basis for many technical applications in optics, information processing and storage, and medicine.

The induced inhomogeneous NLC molecular orientation causes the particle concentration to redistribute within the FN cell. This is the segregation effect, first predicted in Ref. [1]. Ferroparticles transfer inward from of the cell substrates, minimizing their orientational energy. The degree to which the concentration profile compresses is controlled by the entropic elasticity of the ferroparticle solution.

The primary problem with FN's is providing the stability of these systems. It is known [2,3,7] that increasing the stratification of the magnetic suspension with magnetic field causes abrupt local coagulation at a particular critical ferroparticle concentration.

In this paper, we study the effect of adsorption and desorption of the ferroparticles on the macroscopic properties of ferronematics and discuss one way to enhance the stability of these systems.

MODEL

Consider a nematic cell of thickness D filled with FN. The ferroparticles are modelled as rod-like micron-sized monodomain ferrite grains of length L and diameter $d << L$. We suppose here LC homeotropic anchoring, of finite strengths W_0 and W_D at the lower ($z = 0$) and upper ($z = D$) cell planes respectively. We also suppose an initial homeotropic anchoring of finite

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strength W_p of the nematic molecules at the ferroparticle surfaces. To begin with it can be arranged for the ferroparticles to be homogeneously distributed over the cell volume, by using an ultrasound treatment technique to stir up the particles in bulk. The cell is initially subject to a small bias magnetic field H_b parallel to the cell planes. The role of this field is to saturate the ferroparticle magnetisation. This requires that the ratio of magnetic field energy to heat energy be sufficiently large $\rho_b = M_s v H_b / k_B T \geq 10$ [3], where M_s is the saturation magnetization of the colloidal material and v is the volume of the particle. Taking $M_s \sim 340\text{G}$, $v \sim 2 \times 10^{-15}\,\text{cm}^3$ for γ-Fe_2O_3, one finds $\rho_b \geq 10$ at $H_b \geq 0.6$ Oe and $T = 25^\circ\text{C}$.

We consider a case in which the cell boundaries adsorb ferroparticles. Surfactant molecules placed on the cell planes attract the ferroparticles in the bulk. An external magnetic field H normal to the cell planes rotates the ferroparticles, producing distortions within the LC matrix. These induced distortions produce ferroparticle migration toward the centre of the cell as a consequence of the segregation effect. At fixed temperature T and magnetic field H, there will be an equilibrium FN pattern and degree of adsorption.

Figure 1 shows a geometric pattern in an FN cell subject to the external magnetic field $\mathbf{H}_s = \mathbf{H} + \mathbf{H}_b$. In this geometry, the director $\mathbf{n}$ and the unit vector $\mathbf{m}$ in the sample magnetization direction are given by $\mathbf{n} = [\sin\phi(z), 0, \cos\phi(z)]$, $\mathbf{m} = [-\cos\psi(z), 0, \sin\psi(z)]$. The FN equilibrium state can be determined using the continuum theory [1,3], by minimising the full free energy functional F, including both the volume F_v [3] and surface parts F_{si} ($i = 0$ or D):

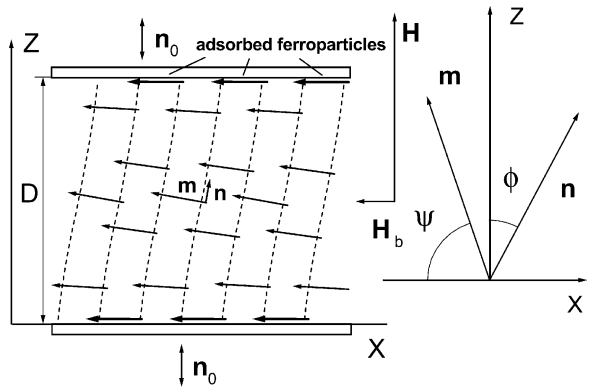

FIGURE 1 Geometric pattern of the FN cell.

$$F_v = \frac{1}{2}\int_0^D \left\{ K_3(p\sin^2\phi + 1)\left(\frac{d\phi}{dz}\right)^2 - \chi_a(H_b\sin\phi - H\cos\phi)^2 \right.$$
$$\left. + 2f\left[\frac{k_BT}{v}\ln f + \frac{W_p}{d}\sin^2(\psi-\phi) - M_s(H\sin\psi + H_b\cos\psi)\right]\right\} dz,$$
$$F_{si} = \frac{W_i}{2}\sin^2\phi_i + f_{si}\left(\frac{k_BT}{S_p}\ln f_{si} + \overline{W}_{pi}\sin^2\phi_i - \frac{v}{S_p}M_sH_b + \frac{E_{ads}^{(i)}}{S_p}\right).$$

The functional $F = F_v + F_{s0} + F_{sD}$ is subject to ferroparticle number conservation

$$\int_0^D f\,dz + (f_{s0} + f_{sD})v/S_p = \bar{f}D, \tag{1}$$

where $\bar{f}$ is the mean volume fraction of the ferroparticles initially in the FN cell. In these equations, $p = K_1/K_3 - 1$, K_j are the nematic elastic (Frank) constants, χ_a is the anisotropic part of the nematic diamagnetic susceptibility, $S_p = Ld$ is the site area, $\overline{W}_{pi}$ is the anchoring strength at the adsorbed ferroparticle surface, $E_{ads}^{(i)}$ is the adsorption energy per particle, and f_{si} is the surface fraction of the adsorbed particles. Note that $f = cv$ and $f_{si} = c_{si}S_p$, where c is the volume number concentration and c_{si} is the surface density of the adsorbed particles. In this work we assume that $f << 1$ and $f_{si} << 1$, the adsorbing surface is homogeneous, and lateral interactions between the adsorbed particles are negligible. Finally we recall that for the soft particle-to-director anchoring under consideration, the surface energy greatly exceeds the energy of local director field distortion near the ferroparticle surfaces [3]. We thus suppose that the local director field distortion in the neighbourhood of the ferroparticles may be disregarded, and the director in our geometry can be considered to be confined to the x-z plane.

We have minimized $F = F_v + F_{s0} + F_{sD}$ in $\phi, \psi, \phi_0, \phi_D, f, f_{s0}$ and f_{sD} using mathematical techniques described in Ref. [3]. We obtain a set of algebraic equations. These are then solved numerically. For f_{si} the resulting equation is

$$f_{si} = f_i e^{-\beta\left(E_{ads}^{(i)} - E_i\right)}, \tag{2}$$

where f_i is the volume particle fraction in the vicinity of the lower $(i = 0)$ or upper $(i = D)$ cell planes, $E_i = (v/d)W_p\sin^2(\psi_i - \phi_i) - S_p\overline{W}_{pi}\sin^2\phi_i - M_sv[H_b(\cos\psi_i - 1) + H\sin\psi_i]$, and $\beta = 1/k_BT$.

In what follows we use parameters intrinsic to this system, with $\lambda = (K_3v/2\bar{f}k_BT)^{1/2}$ (the FN magnetic coherence length [3]) and the following dimensionless parameters: $\rho = M_svH/k_BT$, $\sigma = vW_p/dk_BT$,

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$\bar{\sigma}_i = S_p\overline{W}_{pi}/k_BT$, $w_0 = W_0D/K_3$, $w_D = W_DD/K_3$, $\gamma = DS_p/2v$ and $\kappa = \chi_a k_BT/2\bar{f}vM_s^2$.

NUMERICAL RESULTS AND DISCUSSION

We have performed numerical calculations on the FN system for a wide range of actual system parameters. The procedure was as follows. First we solved numerically the set of equilibrium equations for values ϕ_m, ϕ_0, ϕ_D,f_m,f_{si}; $\psi_m(\phi_m)$ was found using the bonding equation [3]. Here the subscript m refers to values in the plane $z = z_m$ on which the deviation in **n** is maximal. The final step is to compute the equilibrium profiles $\phi(z)$, $\psi(z)$, $f(z)$.

As an illustration, we show in Figures 2 and 3 the results of calculations for a FN cell with $D = 340\,\mu\text{m}$, $\bar{f} = 3 \times 10^{-7}$ and magnetite particles of $d = 70\,\text{nm}$ and $L = 500\,\text{nm}$. Using the experimental parameters $K_3 = 7.5 \times 10^{-7}$ dyn and $\chi_a = 0.97 \times 10^{-7}$ [8] and taking $T = 25^\circ$, we have $D/\lambda = 0.14$, $\gamma = 3150$, and $\kappa = 2.9 \times 10^{-5}$.

For $W_p = 5.1 \times 10^{-2}\text{erg cm}^{-2}$, compatible with known values for real systems [3,8], one finds $\sigma = 350$. In our calculations we assumed that $\bar{\sigma}_0 = \bar{\sigma}_D \equiv \bar{\sigma} = \sigma/2$, $w_0 = w_D \equiv w$, and $E_{ads}^{(0)}/k_BT = E_{ads}^{(D)}/k_BT \equiv E_a$. Under these conditions $f_{s0} = f_{sD} \equiv f_s$.

Computations were performed for the interval of interest $w \geq 3$ (soft and strong anchoring) and $E_a \geq -10$. Figure 2(a) shows the effect of adsorption/desorption of ferroparticles on the extent of distortion of a

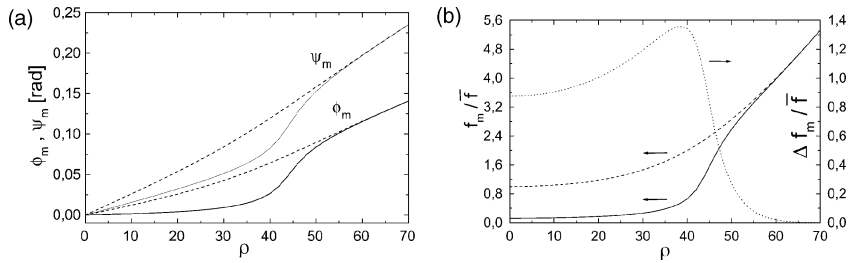

FIGURE 2 The normalized magnetic field dependence of (a) the angle of maximum deviation of the nematic director, ϕ_m, and the corresponding angle of the ferroparticle rotation, ψ_m, and (b) the normalized volume particle fraction at $\rho_b = 10$, $w = 1000$, $p = 0$ and $E_a = -10$ (solid lines) and in the absence of the adsorption (dashed lines). $\Delta f_m/\bar{f}$ is the difference in the normalized volume particle fractions.

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NLC matrix. Competition of adsorption and segregation manifests itself in the fact that the segregation falls in weak magnetic fields as compared to the case when there is no adsorption (Fig. 2(b)). However, as magnetic field increases, the segregation grows and adsorption falls for depletion of the near-surface layers in ferroparticles. A slow growth of the NLC matrix distortion with field changes to a rapid increase, and subsequently slows down. The two processes compete, and the magnitude of ρ is such that the adsorption effect peaks. This is exemplified by Figure 2(b).

Figure 3 shows profiles $f(z)$, $\phi(z)$ and $\psi(z)$ corresponding to points in the curves in Figure 2 such that $\rho = 40$. These profiles in weak magnetic fields (i.e. $\rho << \sigma$) can be approximated by equations

$$f/\bar{f} = \frac{\theta}{1 - \frac{\rho^2 D^2}{48\lambda^2}\theta}\left[1 - \frac{\rho^2 D^2}{16\lambda^2}\theta\left(1 - 2\frac{z}{D}\right)^2\right], \tag{3}$$

$$\phi = \frac{\rho D^2}{4\lambda^2}\theta\left[A + \frac{z}{D} - \left(\frac{z}{D}\right)^2\right], \tag{4}$$

$$\psi = \phi + \frac{\rho}{2\sigma}, \tag{5}$$

where, in keeping with the ferroparticle number conservation (Eq. (1)),

$$\theta = 1 - \frac{f_s}{\bar{f}} = \frac{1}{D\bar{f}}\int_0^D f\,dz = \frac{N}{\bar{N}}, \tag{6}$$

is the ratio of the ferroparticle number inside the FN cell to the total ferroparticle number; $A = 1/[w + \bar{\sigma}D^2(1-\theta)/2\lambda^2]$. The value of θ can be calculated for given ρ numerically from the equation

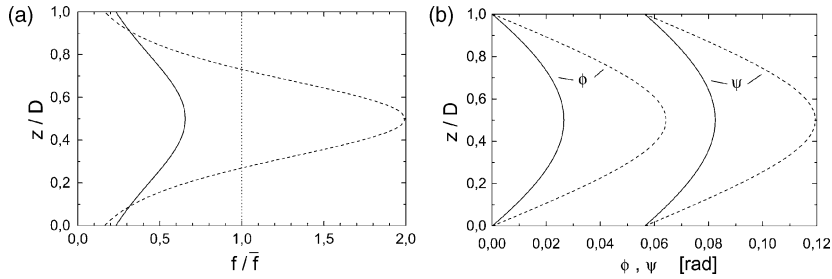

FIGURE 3 Concentration (a) and orientational (b) profiles inside the FN cell at $\rho = 40$, $\rho_b = 10$, $w = 1000$, $p = 0$, and $E_a = -10$ (solid lines) and in the absence of the adsorption (dashed lines).

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$$(1-\theta)\gamma = \frac{\theta}{1-\frac{\rho^2 D^2}{48\lambda^2}\theta} e^{-[(\rho/\rho^*)^2+E_a]}, \tag{7}$$

where

$$\rho^* = \frac{2\sigma^{1/2}}{\sqrt{1+\frac{D^2\sigma}{\lambda^2}\left(\frac{1}{w}+\frac{1}{4}\right)}}.$$

The numerical modelling indicates that in actual FN systems the adsorption phenomenon should manifest itself in region of small, $\rho < \sigma$, magnetic fields ($0 \leq \rho < 65$ in the case considered above). An increase of σ and/or w (anchoring in particular) or a decrease of D/λ (cell thickness in particular) implies an extension of the range of ρ where the effect appears. This is also apparent from Eq. (7) once it is realised that $\theta \to 1$ as $\rho \to \sigma$.

It is pertinent to recall that in order for our calculations to be valid, the condition $D\sigma^{1/2}/\lambda > 1$ [9] must be fulfilled; this ensures ferroparticle collective behavior. Finally, all the features discussed above turn out to be essentially independent of bias magnetic field H_b and of the nematic diamagnetic susceptibility over the range of magnetic fields studied.

CONCLUSIONS

External magnetic fields control the adsorption and desorption of ferroparticles in a ferronematic cell. We have investigated the effect of this phenomenon on macroscopic ferronematic properties. Adsorption and desorption appear in weak magnetic fields ($\rho < \sigma$) and reduce the degree of distortion of the LC matrix in the magnetic field. As this takes place, the segregation effect falls and the ferroparticles become less likely to coagulate. The range of magnetic fields H over which this adsorption/desorption effect occurs can be extended by increasing the system parameters $\sigma \sim W_p/d$, $w_i \sim W_i$ ($i = 0$ or D) and K_3, or by decreasing $D\bar{f}$. In our calculations we have by necessity employed a simplified adsorption theory. We hope that the present results will stimulate more detailed theoretical calculations and experiments.

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