The structural transitions in liquid crystals doped with fine magnetic particles

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The stable ferronematics and ferrosmectics (combination of liquid crystals with fine magnetic particles) were prepared for 8CB liquid crystal and magnetic particles 11 nm in diameter. The structural transitions, i.e. magnetic Fredericksz transition, were indicated by means of dielectric and conductivity measurements. The experimental results, i.e. the proof of initial condition $\vec{n}_0 \perp \vec{m}_0$ ($\vec{n}_0$ is the director of LC molecules and $\vec{m}_0$ is the magnetic moment of particles) and the increase of the threshold field of Fredericksz transition vs volume conduction of magnetic particles, are in qualitative agreement with the Burylov and Raikher theory of thermotropic ferronematics.

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1 Introduction

The combination of liquid crystals and magnetic fluids gives interesting materials; the so-called ferronematics, ferrosmectics and ferrocholesterics. Brochard and de Gennes constructed a continuum theory of magnetic suspensions in a liquid crystal in their fundamental paper [1], prior to the chemical synthesis of these materials. In the first experimental paper, Rault et al. [2] reported the basic magnetic properties of a suspension of rod-like γ-Fe_2O_3 particles in an MBBA liquid crystal. Later, on the basis of estimates given in [1], first lyotropic [3,4] and then thermotropic [5,6] ferronematics were prepared and studied. In a theoretical paper [7], Burylov and Raikher analyzed the Brochard-de Gennes theory and gave the limitations of its applicability to real thermotropic systems. The main difference between the above theories lies in the fundamental fact that in thermotropic ferronematics with finite anchoring on particles, the equilibrium orientational stated is $\vec{n}_0(\vec{r}) \perp \vec{m}_0(\vec{r})$ (where $\vec{n}_0(\vec{r})$ is the initial director of the nematic molecules and $\vec{m}_0(\vec{r})$ is the local magnetization), and not $\vec{n}_0(\vec{r}) \parallel \vec{m}_0(\vec{r})$ (the co-alignment postulate). Burylov and

Raikher [8] studied the magnetic Fredericksz transition (the instability of a uniform texture) and derived the increase in the threshold magnetic field of thermotropic ferronematics H_{FN} in comparison with the threshold field of pure liquid crystal H_{LC}. The obtained approximate formula has the form

$$H_{\mathrm{FN}}^2 - H_{\mathrm{LC}}^2 = 2\frac{Wf}{\chi_{\mathrm{a}} d}, \tag{1}$$

where $H_{\mathrm{LC}} = (\pi/D)(K/\chi_{\mathrm{a}})^{1/2}$, d is the magnetic particle size, f is the volume concentration of magnetic particles, D is the thickness of ferronematic layer, K is the corresponding elastic constant, χ_{a} is the anisotropy part of the nematic liquid carrier diamagnetic susceptibility, and W stands for the surface density of the anisotropic part of interfacial energy at the magnetic particle-nematic boundary. The aim of this work was to prepare stable 8CB based ferronematics (ferrosmectics) to prove or not the initial condition $\vec{n}_0 \perp \vec{m}_0$ and study the magnetic Fredericksz transition. The experimental results will be discussed in the frame of Burylov and Raikher theory [8].

2 Theory

In addition to the Fredericksz transition we have studied the influence of external magnetic field, directed parallel to the initial director, on the equilibrium ferronematic texture, Fig. 1. Such orientation of magnetic field provokes the rotation of magnetic particles towards the field direction, but it also supports the initial director orientation. This could disturb the assumed perpendicularity between $\vec{n}$

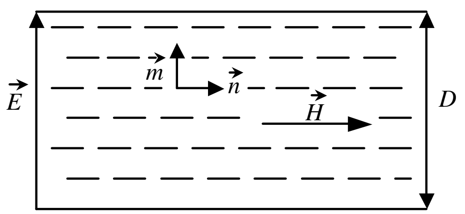

Fig. 1. The initial texture of the ferronematic cell, magnetic field is parallel to the nematic director, i.e. $\vec{n} \parallel \vec{H}$. $\vec{E}$ indicates the direction of the measuring electric field.

and $\vec{m}$. Thus it is interesting to study the behavior of the magnetic moment-director system depending upon the magnetic field growth. The total free energy of the ferronematic, supposing the homeotropic soft anchoring of nematic molecules on the particle surfaces and taking into account the two dimensional geometry with

$$\vec{n} = (\cos\varphi\,(z,H)\,, 0, \sin\varphi\,(z,H))\,,$$

$$\vec{m} = (\cos\psi\,(z,H)\,, 0, \sin\psi\,(z,H))\,,$$

$$\vec{H} = (H, 0, 0)$$

is represented by the formula

$$F = \frac{1}{2}\left[K_1\left(\frac{\partial \sin\varphi}{\partial z}\right)^2 + K_3\left(\frac{\partial \cos\varphi}{\partial z}\right)^2\right] - \frac{1}{2}\chi_\mathrm{a} H^2 \cos^2\varphi$$
$$- M_\mathrm{s} f H \cos\psi + \frac{f k_\mathrm{B} T}{v}\ln f + \frac{W f}{d}\cos^2(\psi - \varphi)\,, \tag{2}$$

where K_i are the Frank orientation-elastic moduli of the nematic matrix, χ_a is the anisotropic part of the NLC diamagnetic susceptibility, M_s is the saturation magnetisation of particle material, f is the particle volume fraction, v is the volume of the particle, W is the surface density of the anchoring energy and d is the particle diameter. The equation describing the equilibrium state of the system was then found in the form

$$K_3\left(\frac{\partial\varphi}{\partial z}\right)^2\left(1 + \frac{K_1 - K_3}{K_3}\sin^2\varphi\right) = \frac{1}{2}\left(\frac{\chi_\mathrm{a} H^2}{2} - \frac{2Wf}{d}\right)\cos 2\varphi. \tag{3}$$

The left side of (3) is always positive, thus we have obtained

$$\chi_\mathrm{a} H^2 < \frac{2Wf}{d} \quad \wedge \quad \varphi \in \left(-\frac{\pi}{2}, -\frac{\pi}{4}\right), \tag{4}$$

$$\chi_\mathrm{a} H^2 < \frac{2Wf}{d} \quad \wedge \quad \varphi \in \left(-\frac{\pi}{4}, 0\right). \tag{5}$$

This determines the 'critical' value of magnetic field, $H_\mathrm{max} = \sqrt{2Wf/\chi_\mathrm{a} d}$, at which the initial perpendicularity between $\vec{n}$ and $\vec{m}$ breaks down and the director follows the magnetic field direction.

3 Experimental methods

The used 8CB liquid crystal with the general formula $CH_3(CH_2)_7(C_6H_4)_2CN$ has a liquid crystal phase (smectic A and nematic) between 21° and 40°C. Magnetic Fe_3O_4 particles used in the ferronematics were of the mean diameter $D_v = 11\,\mathrm{nm}$ and with standard deviation $\sigma = 0.28$. After their preparation by a well-known precipitation technique they were coated with the surfactant (oleic acid) for suppressing their aggregation. The shape of the particles was observed using an electron microscope as nearly spherical. The doping of nematic sample with magnetic suspension was simply done by adding this suspension to the liquid crystal under continuous stirring. Our measurements were performed with ferronematics with volume concentrations of magnetic particles $\varphi_1 = 10^{-4}$, $\varphi_2 = 10^{-3}$, $\varphi_3 = 5 \times 10^{-3}$, and $\varphi_4 = 10^{-2}$, respectively. The results were reproducible after one half year of measurements with the same samples. The magnetic Fredericksz transition was indicated by dielectric and conductivity measurements, which were performed in a capacitor (obtained from LINCAM co.) with glass electrodes covered by a thin gold film and a substance guaranteeing the planar orientation of liquid crystal molecules. The alignment in the bulk was the same due to the orientational-elastic interactions. The capacitor was connected to a regulated thermostat system. The distance between the electrodes, determining the sample thickness, was $D = 18\,\mu$m. The capacitances and conductivities were measured using precision RLC-bridge with the accuracy of 0.01%, at the frequency of 2 kHz. The temperature was stabilized with the accuracy of 0.01°C. In the experiment the initial planar alignment of liquid crystal molecules was used, i.e., the director is parallel to the capacitor electrodes. It should be pointed out for the next consideration that the minimum of capacity is observed for planar alignment while the maximum for homeotropic alignment, i.e., the director $\vec{n}(\vec{r})$ is perpendicular to the capacitor electrodes.

4 Results and discussion

For the proof of initial condition $\vec{m}_0(\vec{r}) \perp \vec{n}_0(\vec{r})$ we applied the external magnetic field parallel to the director, i.e. $n_0(\vec{r}) \parallel \vec{H}$. The typical curve of capacity vs the applied magnetic field is illustrated in Fig. 2, where maximum $H_{\max}$ is observed and

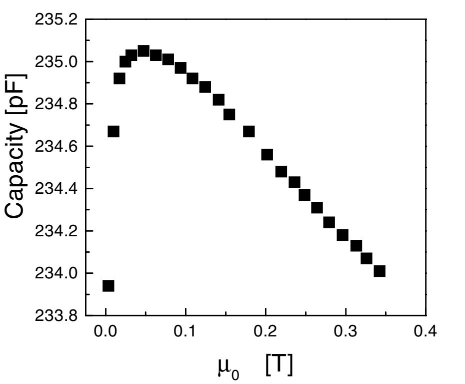

Fig. 2. The capacity vs applied magnetic field for 8CB-based ferronematic ($\varphi = 10^{-3}$) at $t = 36$°C. Magnetic field is parallel to nematic director i.e. $\vec{n} \parallel \vec{H}$.

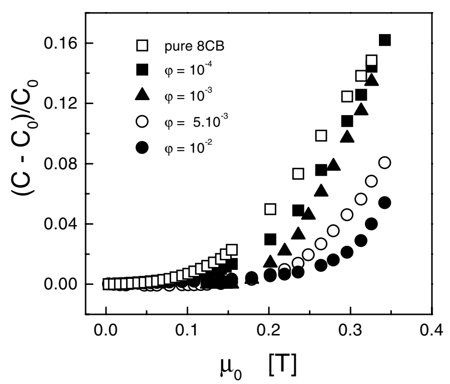

Fig. 3. The magnetic Fredericksz transition for 8CB-based ferronematics at $t = 36$°C; dielectric measurements.

the return of capacity to initial value for large magnetic fields. This is in agreement with the theoretical assumption, considering ‘critical’ magnetic field to correspond to the $H_{\max}$ value.

For the study of magnetic Fredericksz transition the magnetic field was applied perpendicularly to the director $\vec{H} \perp \vec{n}_0(\vec{r})$. The illustration of Fredericksz transition is given in Fig. 3 and the results are summarized in Table 1. The increase of threshold field vs volume concentration of magnetic particles is seen there. This is

Table 1. The threshold fields of magnetic Fredericksz transition for 8CB liquid crystal doped with fine magnetic particle.

Sample	Nematic phase $\mu_0 H$ (mT)		Smectic phase $\mu_0 H$ (mT)	
	$t = 36°$C	$t = 33°$C	$t = 32.4°$C	$t = 31°$C
pure 8CB	162.3	250.6	256.0	258.5
φ_1	218.5	258.2	258.6	265.1
φ_2	225.8	264.9	264.6	269.4
φ_3	230.3	265.8	266.1	270.2
φ_4	265.5	267.6	266.3	277.2

observable for both nematic and smectic phases. We conclude that our experimental results for 8CB based ferronematics and ferrosmetics are in qualitative agreement with the Burylov and Raikher theory of Fredericksz transition in thermotropic ferronematics.

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