Structural transitions in thermotropic ferronematics†

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The structural instabilities in ferronematics based on different types of liquid crystals, exposed to electric or magnetic fields oriented perpendicular (Fredericksz transition) and parallel to the initial director, were studied within the Burylov and Raikher’s theory. Using the capacitance measurements the critical electric (magnetic) fields \( E_{FN} (B_{FN}) \), corresponding to the Fredericksz transition, and fields \( E_{max} (B_{max}) \), at which the initial perpendicularity between director \( n \) and magnetic moment \( m \) breaks-down in field parallel to the initial director, were found. These values were then used for the estimation of the surface density of the anchoring energy \( W \) of liquid crystal molecules on the magnetic particle surface.

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The orientational order of liquid crystal can be easily controlled by rather weak electric fields (liquid crystal displays), taking advantage of the anisotropy of dielectric permittivity. However, because of the small value of the diamagnetic susceptibility anisotropy \( (\chi_a \sim 10^{-7}) \), magnetic fields used for the same purpose have to reach rather large values \( (\mu_0 H \sim 1 \text{T}) \). In effort to enhance the magnetic susceptibility of liquid crystals the idea of doping them with fine magnetic particles was theoretically introduced by Brochard and de Gennes1, who constructed a continuum theory of magnetic suspensions in nematic liquid crystals (ferronematics) in their fundamental work1, prior to the chemical synthesis of these systems. Rault et al.2 reported the basic magnetic properties of a suspension of rod-like \( \gamma \)-Fe₂O₃ particles in an MBBA liquid crystal. Later, based on the estimations given by Brochard and Gennes1, first lyotropic3,4 and then thermotropic5,6 ferronematics were prepared and studied.

An important question solved in the theory of magnetic suspensions in liquid crystals was that of the equilibrium orientation of the magnetization of a needle-like magnetic particle with respect to the host liquid crystalline matrix. The Brochard and de Gennes theory1 gave an universal conclusion: the equilibrium particle (and its magnetic moment \( \vec{m} \)) orientation is parallel to the sample director \( \vec{n} \) (co-alignment postulate \( \vec{n} || \vec{m} \)).

Since the later experiments excluded from the presence of co-alignment in thermotropic ferronematics, Burylov and Raikher7,8 re-analysed the Brochard and de Gennes theory and gave the limitation of its applicability. They found a parameter

\[ \omega = \frac{Wd}{K} \quad \ldots (1) \]

determining the type of anchoring present in studied ferronematic – rigid anchoring with \( \vec{n} || \vec{m} \) for ferronematics with \( \omega \gg 1 \) and soft anchoring with \( \vec{n} \perp \vec{m} \) for ferronematics with \( \omega \leq 1 \). The quantities entering this formula are surface density of anchoring energy at the magnetic particle – nematic boundary \( W \), the typical particle size \( d \) and the Frank orientation-elastic modulus of liquid crystal \( K \) (depending on the geometry of the solved problem one or more of the splay, bend and twist moduli are considered).

Further Burylov and Raikher9,10 studied the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric field (magnetic or electric Fredericksz transitions), and found the expressions for their critical fields in different geometries.

The aim of our work was to study the structural instabilities in ferronematics based on different types

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of nematic liquid crystals, exposed to electric or magnetic fields oriented perpendicular and parallel to the initial director. The experimental results were compared with the theoretical estimations obtained following the Burylov and Raikher’s theory.

Theory

Instabilities of ferronematic structure in electric field

The effect of magnetic admixture and bias magnetic field upon the threshold field of electric Fredericksz transition was studied by Burylov and Raikher\textsuperscript{10}. We have modified the expression for the critical electric field\textsuperscript{11} according to the initial ferronematic texture used in our experiments (Fig. 1a). Then we obtained

\[ E_{CFN} = \frac{1}{D|\varepsilon_a|} \sqrt{\pi^2 K_1 + \chi_a D^2 \Lambda}, \quad \ldots (2) \]

where \( \Lambda = G^2(H) - H^2 \) and

\[ G(H) = \left[ \frac{2WfM_H H}{\chi_a (2W + M_H d)} \right]^{\frac{1}{2}} \]

Assuming \( \mu_0 H \geq 10^{-2} T \) we could consider \( W/M_H d < < 1 \), then the expression for \( \Lambda(H) \) reduces to \( \Lambda(H) = 2Wf/\chi_a d - H^2 \). Here \( \varepsilon_a \) is the anisotropy of dielectric permittivity of liquid crystal, \( D \) the thickness of the ferronematic layer, \( f \) the volume concentration of magnetic particles, \( d \) is the particle diameter and \( \chi_a \) the anisotropy of diamagnetic susceptibility.

Concerning Eq. (2) we can expect, that critical field \( E_{CFN} \) will increase with volume concentration \( f \) at constant magnetic field and decrease with increasing magnetic field at constant volume concentration.

Instabilities of ferronematic structure in magnetic field

The approximative formula for the change of the critical field \( B_{FN} \) of magnetic Fredericksz transition in \[ B_{FN}^2 - B_{LC}^2 = 2\mu_0 Wf/\chi_a d, \quad \ldots (3) \]

where

\[ B_{max}^2 = \left( \frac{\pi}{D} \right)^2 \mu_0 K \left| \frac{\chi_a}{d} \right|. \quad \ldots (4) \]

In addition to the magnetic Fredericksz transition, we have studied the influence of the external magnetic field, directed parallel to the initial director orientation (Fig. 1b), upon the equilibrium ferronematic texture. Such orientation of magnetic field provokes the rotation of magnetic particles towards the field direction, but it also supports the initial director orientation. The liquid crystal molecules anchored at the magnetic particles surfaces should follow their movement keeping their perpendicular bonding, but at some field intensity the diamagnetic properties of liquid crystal overcome the initial perpendicular bonding between \( \vec{n} \) and \( \vec{m} \) and the director follows the magnetic field direction. In the capacitance measurements this manifests in the existence of a capacitance maximum. This maximum corresponds to the director twist, related to the movement of the liquid crystal molecules anchored at magnetic particles, into the direction perpendicular to the capacitor electrodes and to the consecutive break-down of the initial perpendicularity between \( \vec{n} \) and \( \vec{m} \) (director follows the field direction parallel to the electrodes). Magnetic field corresponding to this capacitance maximum was found as

\[ B_{max}^2 = \frac{2\mu_0 Wf}{|\chi_a| d} \quad \ldots (5) \]

The experimentally obtained values \( B_{FN} \) and \( B_{max} \) can be used for the estimation of the surface density of anchoring energy \( W \) of liquid crystal molecules on the magnetic particle surface.

Experimental Procedure

The structural instabilities in external electric and magnetic fields were studied in ferronematics based on liquid crystals 8CB (the nematic-isotropic transition at 15°C), 7CP5BOC (15°C) and ZLI-1695 (15°C). Magnetic Fe\textsubscript{3}O\textsubscript{4} particles
were of the mean diameter \( D_c = 11 \text{ nm} \), standard deviation \( \sigma = 0.28 \). After their preparation by the precipitation technique they were coated with the surfactant (oleic acid) for suppressing their aggregation. The shape of the particles was observed using the electron microscope as nearly spherical. The dopping of the nematic sample with magnetic suspension was simply done by adding this suspension, under continuous stirring, to liquid crystal in isotropic phase. The homogeneity and stability of the sample were verified using optical microscopy (aggregates of 1 \( \mu \text{m} \) and larger size can be detected) and dielectric measurements. It is known, that the dielectric properties of very diluted magnetic colloids depend on the volume concentration and dispersion of magnetic particles. It was shown, that the anisotropy parameter, defined as

\[
g(H) = \frac{\varepsilon_{II}(H) - \varepsilon_0}{\varepsilon_{||}(H) - \varepsilon_0}
\]

reaches in well diluted dispersed magnetic colloids the constant value \( g(H) = 2 \). The presence of aggregates violates this equality. Our measurements of \( g(H) \) (intensity \( H \) had to be lower than that invoking the change of liquid crystal molecules orientation), performed in samples with volume concentrations of magnetic particles \( f = 10^{-2}-10^{-3} \) (accuracy up to \( \pm f \)), gave \( g(H) \geq 2 \), what was an indirect proof of the absence of aggregation in studied samples. In samples with \( f = 10^{-4}-10^{-5} \) the minute capacitance changes could not be detected due to the accuracy of the capacitance measurements.

In the ZLI 1695-based ferronematic with \( f = 10^{-2} \), the anisotropy parameter was found to be \( g(H) = 1.6 \), thus in this sample the aggregates could be present.

The measurements were performed with ferronematics with different volume concentrations of magnetic particles. The structural instabilities of the ferronematic texture were indicated by capacitance measurements, which were performed in a capacitor (obtained from LINCAM co.) with glass electrodes covered by conductive polymeric film guaranteeing the planar orientation of liquid crystal molecules. The capacitor with the electrode area 1 cm \( \times \) 1 cm was connected to a regulated thermostat system, the temperature was stabilized with the accuracy of 0.1°C. The distance between the electrodes, determining the sample thickness, was \( D = 18 \mu \text{m} \). The capacitances were measured using the precision RLC-bridge with the accuracy of 0.01%, at the frequency of 2 kHz (in the case of 8CB- and 7CP5BOC-based ferronematics) and using the precision capacitance bridge radio general (accuracy to \( \pm f \)) and the lock-in amplifier model 830 DSP at the frequency up to 10 kHz (in the case of ZLI1695-based ferronematic). In all experiments the initial planar alignment of liquid crystal molecules was used, i.e., the director was parallel to the capacitor electrodes (Fig. 1). The planar alignment of liquid crystal molecules was checked up by the capacitance measurements of \( C_0 \) (capacitance of “empty” capacitor), \( C_{||} = \varepsilon_{||} C_0 \) and \( C_{\perp} = \varepsilon_{\perp} C_0 \) of samples with homeotropic and planar alignment and of the capacitance at the Fredericksz transition, as well as magnetic Fredericksz transition and structural instability, provoked by magnetic field applied parallel to the initial director orientation, were investigated in the 8CB-based ferronematic.

The theoretically predicted Eq. (2) increase of the electric critical field with the particle volume concentration as well as its decrease with magnetic field growth were experimentally proved (Table 1).

<table>
<thead>
<tr>
<th>( t(\degree C) )</th>
<th>( U_{\text{CFN}}[V]=U_{\text{CFN}}^* )</th>
<th>( f_{\perp}=10^{-3} )</th>
<th>( f_{\perp}=10^{-4} )</th>
<th>( f_{\perp}=6.10^{-3} )</th>
<th>( f_{\perp}=6.10^{-4} )</th>
</tr>
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<tr>
<td>32.4</td>
<td>0.83</td>
<td>0.67</td>
<td>3.95</td>
<td>2.61</td>
<td>6.63</td>
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<tr>
<td>32.6</td>
<td>0.82</td>
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<td>0.97</td>
<td>0.79</td>
<td>4.37</td>
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<td>33.0</td>
<td>0.81</td>
<td>0.67</td>
<td>0.87</td>
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<table>
<thead>
<tr>
<th>8CB-Based Ferronematic in ( B=0T ) and ( B=0.786 T ) at Different Temperatures</th>
<th></th>
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<td>0.74</td>
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</table>
The illustration of magnetic Fredericksz transition in Fig. 2 shows the increase of the critical field with volume concentration of magnetic particles Eq. (3), the found values of critical magnetic fields are presented in Table 2.

Concerning the structural instability in external magnetic field applied parallel to the initial director orientation, the expected curve of capacitance versus applied magnetic field was observed (Fig. 3). The capacitance maximum corresponding to the field $B_{\text{max}}$ and then the return to initial value for large magnetic fields is obvious.

7CP5BOC-based ferronematic
The magnetic Fredericksz transition was also studied in the 7PC5BOC-based ferronematic. The obtained results are presented in Fig. 4 and Table 2. It is evident that in this case the magnetic admixture shifts the magnetic critical field to lower values. This corresponds to the soft anchoring of liquid crystal molecules on the particle surface with the boundary condition $n \parallel m$ considered by Burylov and Raikher $^8$.

ZLI-1695-based ferronematic
In contrast to liquid crystals used in the above mentioned ferronematics, ZLI-1695 has extremely low and negative anisotropy of diamagnetic susceptibility $\chi_a = -3 \times 10^{-8}$. According to the negative value of $\chi_a$, the decrease of critical magnetic field with increasing volume concentration of magnetic particles can be predicted considering Eq. (3). Due to the negative value of $\chi_a$, the magnetic Fredericksz transition was invoked using magnetic field oriented parallel to the initial director orientation (Fig. 1b). The known values of $\chi_a$ allowed to estimate, by means of the experimentally obtained values $B_{\text{FN}}$, the surface density of the anchoring energy $W$ and parameter $\omega$. The obtained dependences of the FN cell capacitance upon magnetic field are presented in Fig. 5.

The critical magnetic field corresponding to the Fredericksz transition in pure liquid crystal was found to be $B_{\text{LC}} = 5.24$ T. Using the expression for $B_{\text{LC}}$ Eq. (4) the value of the splay elastic constant $K_{11}$ was

<table>
<thead>
<tr>
<th>Volume concentration of magnetic particles</th>
<th>Pure LC</th>
<th>$f_1=10^{-4}$</th>
<th>$f_2=10^{-3}$</th>
<th>$f_3=10^{-2}$</th>
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<tbody>
<tr>
<td>8CB $t=36^\circ$C</td>
<td>162.3</td>
<td>218.5</td>
<td>225.8</td>
<td>265.5</td>
</tr>
<tr>
<td>7CP5BOC $t=26^\circ$C</td>
<td>Pure LC</td>
<td>$f_1=2\times10^{-5}$</td>
<td>$f_2=3\times10^{-5}$</td>
<td>$f_3=4\times10^{-5}$</td>
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<tr>
<td>8CB $t=36^\circ$C</td>
<td>95.9</td>
<td>60.6</td>
<td>44.9</td>
<td>34.2</td>
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</table>
calculated as $K_{11} = 9.56 \text{ pN}$. The values of the magnetic Fredericksz transition critical fields found for four different magnetic particles volume concentrations are summarized in Table 3. The decrease of the critical magnetic field with increasing volume concentration of magnetic particles is evident. Using $B_{FN}$ the values of the surface density of anchoring energy $W$ of the liquid crystal molecules on the magnetic particle surface were calculated. They fell into the range considered earlier and are also presented in Table 3.

The last column of Table 3 presents the dimensionless parameters $\omega = Wd/K$. For the magnetic particles volume concentrations $f_1$--$f_4$ they are in range $(2.1$-$5.5) \times 10^{-3}$. This means, that in the studied ferroelectric$^7$ the soft-anchoring ($\omega < 1$) of the liquid crystal molecules on the magnetic particles surfaces is present. A low value of $\omega$ ($\sim 10^{-4}$) was found in the sample with $f_4 = 10^{-2}$. Also the curve of the lock-in signal corresponding to this volume concentration, which shows a nice sharp change (Fig. 5), differs from the curves obtained at lower volume concentrations. The volume concentration $f_4$ seems to be rather high, the concentrations considered in

Burylov and Raikher’s theory are of $10^{-4}$-$10^{-3}$ order. So the aggregation of magnetic particles may be present in this sample.

Conclusions

All obtained experimental results were in agreement with theoretical estimations obtained in frame of the the Burylov and Raikher’s theory, which considers the soft anchoring of liquid crystal molecules to the magnetic particles in thermotropic ferroelectric materials.

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References