The sensitivity of ferronematics to external magnetic fields

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Abstract. The stable colloidal suspensions of nematic liquid crystals with magnetic nanoparticles are called ferronematics. Their behaviour in magnetic field depends on an anchoring energy, volume concentrations of magnetic nanoparticles and sign of anisotropy of diamagnetic susceptibility of liquid crystal as well as on the initial orientation between director (n) of liquid crystal and magnetic moment (m) of magnetic nanoparticles. In this work we present structural changes in ferronematics based on two kinds of liquid crystals: 6CHBT (positive anisotropy of diamagnetic susceptibility) and ZLI1695 (negative anisotropy of diamagnetic susceptibility) exposed to high magnetic fields. In both cases the parallel initial orientation between director and magnetic moments is fulfilled. The density of anchoring energy between liquid crystal molecules and magnetic particles was determinated by Burylov and Raikher’s theory. In the case of 6CHBT-based ferronematics the decrease while in the case of ZLI1695-based ferronematics the increase of the critical magnetic field were observed.

1. Introduction
Ferronematics are stable colloidal suspensions of fine magnetic particles in nematic liquid crystals. They attract considerable interest of investigation because their response to an external magnetic field exceeds sufficiently that of pure nematics. The idea of doping liquid crystals with fine magnetic particles was theoretically introduced by Brochard and de Gennes [1]. The most essential feature of these systems is a strong orientational coupling between the magnetic particles and the liquid crystal matrix. They predicted rigid anchoring with \( m \parallel n \), where the unit vector \( n \) (director) denotes the preferential direction of the nematic molecules and the unit vector \( m \) denotes orientation of magnetic moment of the magnetic particles. Based on the experiments, which excluded the presence of parallel orientation of \( m \) and \( n \) in thermotropic ferronematics, the Burylov and Raikher’s theory was constructed [2, 3]. This theory considers the finite value of the surface density of anchoring energy \( W \) at the nematic - magnetic particle boundary. The finite value of \( W \), as well as the parameter \( \omega \) that is defined as a ratio of anchoring energy to elastic energy of liquid crystal (\( \omega = Wd/K \), where \( d \) is size of the magnetic particles and \( K \) is corresponding orientational-elastic Frank modulus), characterize the type of anchoring of nematic molecules on magnetic particle surface. The parameter \( \omega >> 1 \) characterizes the...
rigid anchoring. The soft anchoring is characterized by parameter \( \omega \leq 1 \) and permits both types of boundary conditions \((m || n \text{ and } m \perp n)\). Thus the Burylov and Raikher’s theory should be applied for thermotropic ferronematics. In its frame the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric field (Fredericksz transitions)\([4, 5]\) should be studied and the expressions for their critical fields in different geometries have been derived. In this work we compare two types of ferronematics based on the liquid crystals 4-(trans-4’-n-hexylecyclohexyl)-isothiocyanatobenzene (6CHBT) and 4-alkyl-4’-cyanobicyclohexyl (ZLI1695) with positive and negative anisotropy of diamagnetic susceptibility, respectively. The aim was to investigate influence of presence the magnetic nanoparticles on the sensitivity of ferronematics with different anisotropy of diamagnetic susceptibility to an external magnetic field.

2. Experiment

The synthesis of the spherical magnetic nanoparticles was based on co-precipitation of Fe\(^{2+}\) and Fe\(^{3+}\) salts by NH\(_4\)OH at 60\(^\circ\)C [6]. The studied ferronematic samples were based on the thermotropic nematics 6CHBT and ZLI1695. The 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [7]. The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is \(T_{N-I} = 42.8\, ^\circ\)C. The splay elastic constant \(K_{11} = 6.7\) pN and the anisotropy of dielectric permittivity \(\epsilon_a = 7\) and the anisotropy of diamagnetic susceptibility \(\chi_a = \chi_\parallel - \chi_\perp = 4.805 \times 10^{-7}\) at temperature 35\(^\circ\)C. The ZLI1695 was obtained from Merck co. The temperature of the nematic-isotropic transition was found to be \(T_{N-I} = 73.5\) \(^\circ\)C. The splay elastic constant \(K_{11} = 7\) pN and the anisotropy of diamagnetic susceptibility \(\chi_a = \chi_\parallel - \chi_\perp = -2.55 \times 10^{-8}\) at temperature 35\(^\circ\)C. All samples were measured at this temperature. The magnetic Fe\(_3\)O\(_4\) particles used in the ferronematics were coated with the surfactant (oleic acid) for suppressing their aggregation. The doping was simply done by adding this suspension, under continuous stirring, to the liquid crystal in the isotropic phase. The ferronematic samples were prepared with different volume concentrations of the magnetic particles \((\phi_1 = 2 \times 10^{-4}, \phi_2 = 5 \times 10^{-4} \text{ and } \phi_3 = 1 \times 10^{-3})\). The volume concentration is usually very low due to not to destroy properties of liquid crystal. The structural transitions in ferronematic samples were indicated by capacitance measurements in a capacitor made of ITO-coated glass electrodes (LINCAM Co.). The capacitor with the electrode area approximately 1cmx1cm was connected to a regulated thermostat system. The distance between the electrodes (sample thickness) was \(D = 5\mu m\) in the case of 6CHBT and \(D = 18\mu m\) in the case of ZLI1695. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling. In the experiment, the initial planar alignment of liquid crystal molecules was used, i.e. the director was parallel to the capacitor electrodes (see Fig. 1). To induce reorientation of liquid crystal molecules the magnetic field was applied perpendicular to the director in the case of 6CHBT due the positive diamagnetic anisotropy while in case of ZLI1695 parallel to the director due to the negative diamagnetic anisotropy.

3. Results and discussion

The observations of the structural transitions in ferronematics in external magnetic field is used to determine of the type of anchoring of nematic molecules on magnetic particle surfaces as well as the surface density of the anchoring energy \(W\) at the nematic - magnetic particle boundary. The dependence of the measured capacitance on the external magnetic field reflects the re-orientation of the nematic molecules in the strong magnetic field.

In both experiments the parallel initial orientation of director \(n\) and magnetic moment \(m\) of magnetic particles was supposed. In order to allow an easier comparison of the behaviour of various samples it is convenient to introduce a reduced capacitance \(C_r\) by formula...
\[ C_r = \frac{(C - C_0)}{(C_{\text{max}} - C_0)}, \]  

where \( C \) is capacitance measured at a magnetic field \( B \), \( C_{\text{max}} \) is its largest value, and \( C_0 \) is its value at \( B = 0 \).

In the experiments with 6CHBT liquid crystal and 6CHBT-based ferronematics liquid crystal the external magnetic field was applied perpendicular to the capacitor electrodes, i.e. perpendicular to the director. As the intensity of applied magnetic field increases the magnetic particles and molecules turns towards its direction. In capacity measurements this manifests the maximum of capacity. Fig. 2 shows reduced capacity dependence on magnetic field of 6CHBT liquid crystal and 6CHBT-based ferronematics with different volume concentration of magnetic nanoparticles. It is clear seen that the critical value of magnetic field \( B_{FN} \) decreases with increasing volume concentration of magnetic particles. In this case, the presence of magnetic particles helps to change orientation of liquid crystal molecules with magnetic field.

![Figure 1](image-url)

**Figure 1.** Cross section of the cell in the initial state and after application of the magnetic field \( B > B_{FN} \) (a) 6CHBT-based ferronematic and (b) ZLI1695-based ferronematic.

In the experiment with ZLI1695 liquid crystal and ZLI1695-based ferronematics, the external magnetic field was oriented parallel to the initial director orientation. As the intensity of magnetic field increases at some intensity \( B_{FN} \) its molecules turns perpendicular to the direction of magnetic field due to negative diamagnetic susceptibility of the liquid crystal, but magnetic moment of magnetic particles remains oriented to the direction of the magnetic field. The initial parallel orientation between magnetic moment of magnetic particle and director is broken-down. In capacity measurements this manifests the maximum of capacity. As it is shown in Fig. 3, the critical magnetic field \( B_{FN} \) increases with increasing volume concentration of magnetic particles. Due to bounding between magnetic particles and molecules of liquid crystal, the magnetic particles prevent from turning to the parallel orientation to the direction of magnetic field. These results confirm the parallel initial orientation in both types of ferronematics. The measured values of \( B_{FN} \) have been used to estimate the surface density of the anchoring energy \( W \) of the liquid crystal molecules on the surface of the magnetic particle. The obtained values are order of \( 10^{-5} \) N/m and \( 10^{-6} \) N/m for 6CHBT-based ferronematics and ZLI1695-based ferronematics, respectively. Calculated parameter \( \omega \) was order of \( 10^{-2} \) and \( 10^{-3} \) for 6CHBT-based ferronematics and ZLI1695-based ferronematics, respectively, i.e. \( \omega < 1 \) that characterizes soft anchoring of nematic molecules on the surfaces of magnetic particles.
Figure 2. Reduced capacity dependence on magnetic field for pure liquid crystal 6CHBT and for 6CHBT doped with different volume concentration of magnetic nanoparticles ($\phi_1 = 2 \times 10^{-4}$, $\phi_2 = 5 \times 10^{-4}$ and $\phi_3 = 1 \times 10^{-3}$).

Figure 3. Reduced capacity dependence on magnetic field for pure liquid crystal ZLI1695 and for ZLI1695 doped with different volume concentration of magnetic nanoparticles ($\phi_1 = 2 \times 10^{-4}$, $\phi_2 = 5 \times 10^{-4}$ and $\phi_3 = 1 \times 10^{-3}$).

4. Conclusion
The influence of the magnetic particles admixture on the structural instabilities in 6CHBT and ZLI1695-based ferroelectrics was studied. It was shown that due to doping with magnetic nanoparticles the value of critical magnetic field decreases with increasing volume concentration of magnetic particles in the case of 6CHBT-based ferroelectrics and increases in the case of ZLI1695-based ferroelectrics. Different behaviour is due to different sign of anisotropy of diamagnetic susceptibility (positive in the case of 6CHBT liquid crystal and negative in the case of ZLI1695 liquid crystal). These results confirm parallel initial orientation between the magnetic moment of magnetic particles and the director. The anchoring energies calculated from the experimental results indicate the soft anchoring in both cases. Obtained results are in good agreement with the Burylov and Raikher’s theory.

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