Increasing the magnetic sensitivity of liquid crystals by rod-like magnetic nanoparticles

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Magnetic Fréedericksz transition was studied in ferronematics based on the nematic liquid crystal 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT was doped with rod-like magnetic particles of different size and volume concentration. The volume concentrations of magnetic particles in the prepared ferronematics were \( \phi_1 = 10^{-4} \) and \( \phi_2 = 10^{-3} \). The structural changes were observed by capacitance measurements that demonstrate a significant influence of the concentration, the shape anisotropy, and/or the size of the magnetic particles on the magnetic response of these ferronematics.

**Keywords:** ferronematics; liquid crystals; magnetic particles; phase transition

1. Introduction

Liquid crystalline phases occur as additional, thermodynamically stable states of matter between the liquid state and the crystal state in some materials. They can be characterized by a long-range orientational order of the molecules and, as a consequence, by an anisotropy in their physical properties. Liquid crystals can be oriented under electric or magnetic fields due to the anisotropy of dielectric permittivity or diamagnetic susceptibility [1].

One of the most important findings related to controlling liquid crystals by external fields was the threshold behaviour in the reorientational response of liquid crystals – an effect described by V.K. Fréedericksz [2], and named after him as "Fréedericksz transition". The dielectric permittivity anisotropy of liquid crystals is in general relatively large; thus driving voltages of the order of a few volts are sufficient to control the orientational response. Therefore, most of the liquid crystal devices are driven by electric field. On the other hand, because of the small value of the anisotropy of the diamagnetic susceptibility (\( \chi_a \sim 10^{-7} \)), the magnetic field \( H \) necessary to align liquid crystals have to reach rather large values (\( B=\mu_0 H \sim 1T \)), and therefore, liquid crystal applications using magnetic fields are rather limited. Consequently, the increase of the magnetic sensitivity of liquid crystals is an important challenge, which can potentially broaden the area of applications and may offer an opportunity to develop new devices.

Brochard and de Gennes [3] first suggested the idea that could increase the magnetic sensitivity of liquid crystals theoretically. According to them, colloidal systems called "ferronematics", consisting of nematic liquid crystals doped with magnetic nanoparticles in small concentrations, should respond to low magnetic fields of the order of tens of Gauss. Such small magnetic fields cannot affect the undoped nematics, however, they may be sufficiently strong to align or rotate the magnetic moments of the particles inside the ferronematic suspensions according
to the predictions. This realignment or rotation effect could then be transferred to the host nematic through the coupling between the nanoparticles and the liquid crystal molecules. One has to note here that the realignment of the nematic host was assumed to be entirely determined by the ferromagnetic properties of nanoparticles (not affected by the intrinsic diamagnetic properties of the nematic), since the theory \[3\] predicted a rigid anchoring with \( \mathbf{n} \parallel \mathbf{m} \), where \( \mathbf{n} \) is the unit vector of the preferred direction of the nematic molecules (director), and \( \mathbf{m} \) is the unit vector of the magnetic moment of the magnetic particles.

The first experimental realization of ferronematic materials was carried out by Chen and Amer \[4\]. Later experiments on some other ferronematics have indicated that besides the predicted \( \mathbf{n} \parallel \mathbf{m} \) condition, the case of \( \mathbf{n} \perp \mathbf{m} \) is also possible. To bridge this gap between the theory and experiments, Burylov and Raikher modified the theoretical description by considering a finite value of the surface density of anchoring energy \( W \) at the nematic – magnetic particle boundary \[5, 6, 7, 8\]. The finite value of \( W \), as well as the parameter \( \omega = Wd/2K \) (\( d \) is the mean diameter of the magnetic particles and \( K \) is an orientational-elastic Frank modulus), characterize the type of anchoring of nematic molecules on magnetic particle’s surface. For \( \omega >> 1 \) the anchoring is rigid, while the soft anchoring is characterized by \( \omega \leq 1 \) which (unlike the rigid anchoring) permits both types of boundary conditions, \( \mathbf{n} \parallel \mathbf{m} \) and \( \mathbf{n} \perp \mathbf{m} \).

So far the magnetic nanoparticles have established their wide range of applications. The properties of magnetic nanoparticles significantly depend on their size, shape and structure. Controlling the shape and size of nanoparticles is one of the ultimate challenges in modern material research. These magnetic particles can be made so small that each particle becomes a single magnetic domain, exhibiting abnormal magnetic properties, known as superparamagnetism. Doping liquid crystals with low volume concentration of nanoparticles has been shown to be a promising method to modify the properties of liquid crystals. At such a low amount, nanosized particles do not disturb significantly the liquid crystalline order, hence producing a macroscopically homogeneous structure. However, the particles can share their properties with the liquid crystal host, enhancing the existing properties, or introducing some new properties for the composite mixtures.

### 2. Experiment

Two types of magnetic rod-like particles were prepared through hydrolysis of FeCl\(_3\) and FeSO\(_4\) solutions (molar ratio 2:1) containing urea. To prepare the larger rod-like particles (sample A) 0.6756 g of FeCl\(_3\) · 6H\(_2\)O, 0.3426 g FeSO\(_4\) · 7H\(_2\)O and 0.60 g (NH\(_2\))\(_2\)CO were dissolved in 10 ml of purified, deoxygenated water. The product was added to a flask with reflux condenser, which has been kept at 90-95°C for 12 h, and then cooled to room temperature \[9\]. After the synthesis particles were coated with oleic acid as a stabilizer. In the synthesis of the smaller rod-like particles (sample B), at first, the stabilizer (oleic acid) was ultrasonically dispersed in water to form homogenous micelles. Then, FeCl\(_3\) · 6H\(_2\)O, FeSO\(_4\) · 7H\(_2\)O were dissolved in the above solution. This mixture was added to a flask with reflux condenser and has been heated in water bath for 12 hours at 90-95 °C during which a dark precipitate has been formed. The sample has been cleaned several times by purified and deoxygenated water, and then it has been dried under low pressure at 50 °C for 3 hours \[10\]. Figure \[1\] shows transmission electron microscopic images of the prepared magnetic particles. The diameter of the larger rod-like particles (sample A) was \( d_A = (18 \pm 3) \) nm and their mean length \( L_A = (400 \pm 52) \) nm. The mean diameter and length of the smaller rod-like particles (sample B) were \( d_B = (10 \pm 1) \) nm and \( L_B = (50 \pm 9) \) nm, respectively. Consequently, the mean shape anisotropies of the nanoparticles were...
approximately \( L_A/d_A \approx 22 \) and \( L_B/d_B \approx 5 \) for the two types of samples.

Figure 1: TEM image of (a) the larger rod-like particles with mean diameter of 18 nm and mean length of 400 nm; (b) the smaller rod-like particles with mean diameter of 10 nm and mean length of 50 nm.

The ferronematic samples were based on the thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT), which was synthesized and purified at the Institute of Chemistry, Military Technical University, Warsaw, Poland. 6CHBT is a low-temperature-melting enantiotropic liquid crystal with high chemical stability [11]. The phase transition temperature from the isotropic liquid to the nematic phase has been found at 42.6 °C. The doping was done by adding nanoparticles to the liquid crystal in the isotropic phase under continuous stirring.

The structural transitions in the prepared samples were monitored by capacitance measurements in a capacitor made of ITO-coated glass electrodes. The capacitor with the electrode area of approximately 1 cm × 1 cm was placed into a regulated thermostat system, the temperature of which was stabilized at 35°C. The distance between the electrodes (sample thickness) was \( D = 5 \mu m \). The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling.

In the experiment the liquid crystal had a planar initial alignment, i.e. the director was parallel to the capacitor electrodes, and the magnetic field was applied perpendicular to them (see Fig. 2). The dependence of the measured capacitance on the external field reflects the reorientation of the nematic molecules.

3. Results

Results presented in work [12] showed that doping with magnetic particles shaped similarly to the molecules of the host liquid crystal is more effective and thus offers better perspectives for ferronematics in applications where a magnetic field is necessary to control the orientation of the liquid crystal. With the aim to study the influence of the size of the particles on the magnetic response

Figure 2: Cross section of a planar cell with initially parallel \( n \) and \( m \).
Figure 3: Reduced capacitance versus magnetic field (a) for pure 6CHBT and for 6CHBT doped with different rod-like particles and with different volume concentrations of magnetic particles; (b) blowup of the low magnetic field region for the same data.

two kinds of rod-like magnetic particles (sample A and sample B) were prepared as described above. Both ferronematics A and B were based on the nematic 6CHBT, and were doped in two different volume concentrations $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$.

Figure 3(a) shows the magnetic Fréedericksz transition in pure 6CHBT and in ferronematics doped with larger (A) and smaller (B) rod-like particles for both volume concentrations. It demonstrates that the critical magnetic field $B_c$ of the Fréedericksz transition, i.e. the magnetic field that initiates the reorientation of the director toward its direction, is shifted to lower values with increasing the volume concentration, and that $B_c$ is lower for larger particles than for smaller ones at a given $\phi$. For all samples the critical magnetic field was determined from the dependence of $(C - C_0)/(C_{max} - C_0)$ versus $B$, where $C$, $C_0$ and $C_{max}$ are the capacitances at a given magnetic field, at $B = 0$, and at the maximum value of $B$, respectively. $B_c$ was determined by linear extrapolation of data in Fig. 3(a). The obtained critical value of the magnetic field for pure 6CHBT is 2.63 T. In ferronematics $B_c$ is lower, and the values obtained for various samples are listed in Table 1. The reduction of $B_c$ becomes larger if the concentration is increased (in case of the same nanoparticle), as well as, if the nanoparticle is larger (at the same concentration).

Observations of the structural transitions in ferronematics in external field
can be used for the determination of the type of anchoring of nematic molecules on the surfaces of magnetic particles as well as the surface density of the anchoring energy $W$ at the nematic – magnetic particle boundary. By means of the Burylov and Raikher’s expression for the free energy of the ferronematic \cite{7} the formula for the critical magnetic field is

$$B_{c}^{2} - B_{c,FN}^{2} = \frac{2\mu_0 W\phi}{\chi_a d},$$

where $B_c$ and $B_{c,FN}$ are the critical fields for the magnetic Fréedericksz transition of the pure liquid crystal and the ferronematic, respectively, $d$ is the "characteristic size" of the particles (the mean diameter), $\phi$ is the volume concentration of magnetic particles in the liquid crystal, $\mu_0$ is the permeability of vacuum and $\chi_a$ is the anisotropy of the diamagnetic susceptibility of the liquid crystal (for 6CHBT $\chi_a = 4.805 \times 10^{-7}$ at $35^\circ C$).

The calculated values of $W$ and the values of parameter $\omega$ are summarized in Table 1. $\omega$ has been calculated using the same $K_1 = 6.71$ pN elastic constant for all ferronematics as for the pure 6CHBT. In all cases $\omega < 1$ that characterizes soft anchoring of the nematic molecules on the surface of magnetic particles.

| sample | $B_{c,FN}$ (T) | $W$ (Nm$^{-1}$) | $\omega$ |
|--------|----------------|----------------|-------|
| sample A $\phi_1$ | 2.39 | $4.14 \times 10^{-5}$ | 0.055 |
| sample A $\phi_2$ | 2.12 | $8.34 \times 10^{-6}$ | 0.011 |
| sample B $\phi_1$ | 2.52 | $1.08 \times 10^{-5}$ | 0.008 |
| sample B $\phi_2$ | 2.25 | $3.54 \times 10^{-6}$ | 0.003 |

Table 1: Critical magnetic fields measured in the ferronematics and the calculated values of the surface density of the anchoring energy $W$, and of the parameter $\omega$.

In recent works by Podoliak et al. \cite{13}, and Buluy et al. \cite{14} both experimental and theoretical investigations have been reported about the optical response of suspensions of ferromagnetic nanoparticles in nematic liquid crystals on the imposed magnetic field. The authors have measured a linear optical response in ferronematics at very low magnetic fields (far below the threshold of the Fréedericksz transition).

A similar effect was also observed in our dielectric measurements in samples doped with rod-like particles as it is demonstrated in Fig. 3(b). The figure provides a clear evidence for a nearly linear magnetic field dependence of the capacitance in the low magnetic field region.

4. Conclusion We have demonstrated that both the threshold of the magnetic Fréedericksz transition and the dielectric response to low magnetic fields (far below the Fréedericksz transition) depend not only on the volume concentration of the magnetic particles, but also on the size of the particles. According to the results, the larger is the particle, the bigger are the effects (larger decrease of the threshold of the Fréedericksz transition, and more pronounced linear response to low magnetic fields). Since in our experiments the larger particles have also a larger aspect ratio $L/d$, further experiments are needed to clarify whether the volume size, the linear size or the shape anisotropy (i.e. $L/d$) influences primarily the magnitude of the effects.

The other challenging task is to explain the linear dielectric response to low magnetic fields. To our present understanding, within the framework of the
Burylov and Raikher’s continuum theory \[5, 6, 7, 8\], both the magnetic moment of magnetic particle \(m\) and the presence of an initial out-of-plane pretilt angle of the nematic director \(n\) are necessary for a linear \(C(B)\) dependence in the low \(B\) limit. A more detailed theoretical analysis is however, needed to justify this assumption.

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