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Néel and Brownian rotations in ferronematics

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Abstract

The magnetic Freedericksz transition was studied in the liquid crystal 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) doped with spherical magnetite nanoparticles of different size (4.2 nm, 11.4 nm, 31.4 nm and 112.7 nm). The volume concentration of magnetic particles in prepared ferronematics was $\phi = 2 \times 10^{-4}$. The obtained results showed that doping with the magnetic particles with size smaller than the Shliomis size increases the threshold of the magnetic Freedericksz transition while in the case of doping with the magnetic particles with size larger than the Shliomis size a decrease of the threshold of the magnetic Freedericksz transition was observed. In the case of doping with magnetic particles with size comparable with the Shliomis size, both Néel and Brownian rotations are present, however, the Brownian rotation is dominant.

Keywords: liquid crystals; magnetic particles; ferronematics; magnetic Freedericksz transition;

1. Introduction

The study of magnetic fluids has become of increasing interest in recent years due to their multiple applications, ranging from technical to biomedical. Magnetic fluids are colloidal systems consisting of magnetic nanoparticles dispersed in a carrier liquid. The colloidal magnetic particles of magnetic fluids are single domain particles and can be considered to be in a state of uniform magnetization with magnetic moment $\boldsymbol{m}$. The motion of the magnetic moment relative to the particle is described by the Landau-Lifshitz equation [1]. Two modes of the rotation of the magnetic moment of fine single domain magnetic particles in applied external magnetic field are possible in

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magnetic fluids, Brownian and Néel rotation. The rotation of a particle as a whole is called Brownian rotation and its relaxation time is given by

$$\tau_B = \frac{3V_h\eta}{k_BT} \tag{1}$$

where V_h denotes the hydrodynamic volume of the particles (including the surfactant layer and the fluid which moves when the particle rotates), η is the dynamic viscosity of the liquid [1]. On the other hand, if the magnetic moment is rotating inside the particle relative to the crystal structure, the rotation is called Néel rotation and its relaxation time is given by the expression

$$\tau_N = f_0^{-1} exp\left(\frac{KV}{k_BT}\right) \tag{2}$$

where K is the magnetic anisotropy constant of the particles, V is their volume (including the surfactant layer) and f_0 is the Larmour frequency of the magnetization vector in the anisotropy field of the particle [1]. Both relaxation phenomena depend on the particle size. For smaller particles τ_N is smaller than τ_B and the relaxation will take place by the rotation of the moment inside the particle (Néel rotation); for larger particles rotation of the whole particle will occur (Brownian rotation). There exists a critical size of the particles, called Shliomis size, which determine the transition from Néel to Brownian relaxation. For example for magnetite particles of nearly spherical shape, the Shliomis size is approximately 10 nm [2]. If we insert magnetic particles into a liquid crystal to prepare ferronematics to increase the response of liquid crystal to applied magnetic field we expect that the structural changes will depend on the size of the magnetic particles. So according to above mentioned considerations, the aim of this paper was to study this size effect by changing the size of magnetic particles dispersed in the liquid crystal matrix. The size effect was studied in 6CHBT-based ferronematics where the initial parallel orientation between director of the liquid crystal molecules and the magnetic moment of the magnetic particles was found [3].

2. Experiment

The magnetite particles were prepared by different methods to obtain particles of different size.

In the first method (sample M1) 25% of NH_4OH was added to a Fe^{2+}/Fe^{3+} solution at 60℃. In a typical synthesis $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ were dissolved in deionized water and then 25% NH_4OH was added at room temperature.

The second method (sample M2) is based on co-precipitation of Fe_2^+ and Fe_3^+ salts by NH_4OH at 60℃. To obtain Fe_3O_4 precipitate, $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ were dissolved in deionized water by vigorous stirring (the ratio Fe^{3+}/Fe^{2+} was 2:1). The solution was heated to 80℃ and 25% NH_4OH was added.

The third method (sample M3) is based on co-precipitation of ferric and ferrous salts in alkaline media. The $FeSO_4{\cdot}7H_2O$ was mixed with $FeCl_3$ and then aqueous ammonia was added. Precipitation was performed at 90℃.

The fourth method (sample M4) is based on the oxidative alkaline hydrolysis of ferrous ions. In a typical experiment $FeSO_4{\cdot}7H_2O$ was dissolved in distilled water and heated to 90℃. Then KOH and KNO_3 (oxidizing agent) were dissolved in water and added drop-wise (0.2 ml/min) under stirring. The suspension was held at 90℃ during 2 h.

After precipitation the iron oxide nanoparticles were isolated from the solution by magnetic decantation, then filtered with distilled water and, finally, with isopropanol before drying at 40℃ under vacuum. The magnetic properties of all prepared magnetic particles were estimated by magnetization measurements using a vibrating sample magnetometer and the size and morphology of the particles were determined by transmission electron microscopy. The mean diameter of the obtained nearly spherical magnetic particles (given in the parentheses after their name) was determined by fitting a Gaussian to the histograms of the size distribution, as shown in Fig.1, 2, 3

and 4 for M1 (4.2 nm), M2 (11.4 nm), M3 (31.4 nm) and M4 (112.7 nm), respectively.

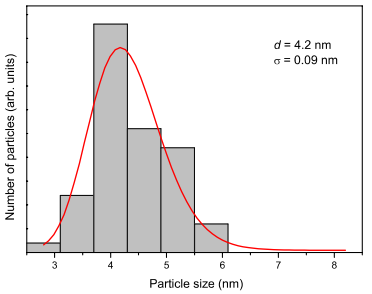

Figure 1: Histogram of size distribution of the magnetic particles M1 (d is meanparticle diameter and σ is standard deviation).

The studied ferronematic samples were based on the thermotropic nematic 4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) which is a low-melting enantiotropic liquid crystal with high chemical stability [4].

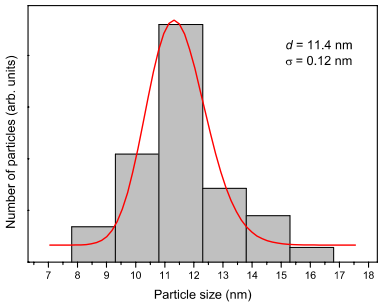

Figure 2: Histogram of size distribution of the magnetic particles M2 (d is meanparticle diameter and σ is standard deviation).

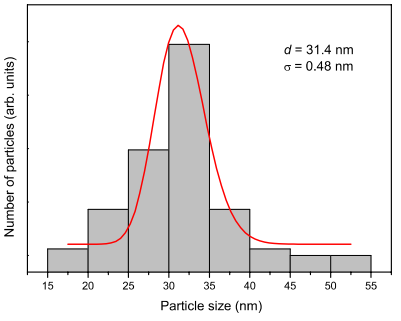

Figure 3: Histogram of size distribution of the magnetic particles M3 (d is meanparticle diameter and σ is standard deviation).

The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is T_{N-I} = 42.8°C. The nematic samples were doped with a magnetic suspension consisting of Fe_3O_4 particles of different size coated with oleic acid as a surfactant. The doping was done by adding this suspension, under continuous stirring, to the liquid crystal in the isotropic phase. Due to the small volume concentrations of the magnetic particles ($2x10^{-4}$) and to the presence of surfactant in the prepared ferronematic samples the interparticle dipole-dipole interactions are avoided. The structural transitions in ferronematic samples were detected by capacitance measurements in a capacitor made of ITO-coated glass electrodes (LINCAM Co.). The capacitor with the electrode area of approximately 1cmx1cm

was connected to a regulated thermostat system; the temperature was stabilized with the accuracy of 0.05 ℃. The distance between the electrodes (sample thickness) was D = 5μm. 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 (Fig. 5). The external magnetic field was applied perpendicular to the director and the classical magnetic Freedericksz transition was studied. All experiments were performed at temperature of 35℃.

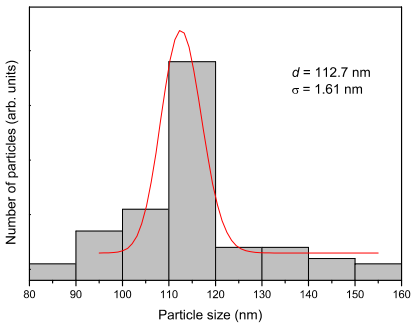

Figure 4: Histogram of size distribution of the magnetic particles M4 (d is meanparticle diameter and σ is standard deviation).

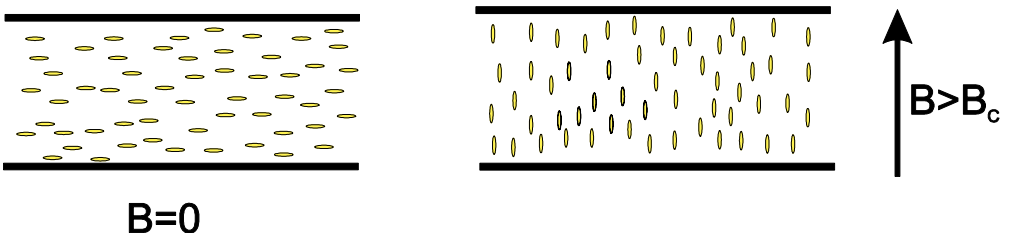

Figure 5: Cross section of the cell in the initial state (left), and after application of the magnetic field $B > B_c$ perpendicular to the surface of the electrodes (right).

3. Result and discussion

If an external magnetic field is applied, one can expect two different kind of behaviour. In the case of particles with their size smaller than the Shliomis size, the magnetic moments will rotate towards the field inside a particles without an actual mechanical motion of particles. Therefore, the liquid crystal molecules anchored on to the surface of the magnetic particles tend to stabilize the initial director alignment, i.e. slightly hinder the magnetic realignment of the liquid crystal. Consequently an increase of the critical magnetic field of the magnetic Freedericksz transition is expected. In contrast to this, when particle's size is larger than the Shliomis size, the magnetic moment will rotate together with the magnetic particle as a whole. Via the anchoring of the liquid crystal molecules at the magnetic particles surface this rotation helps the reorientation of the liquid crystal bulk, hence a decrease of the threshold field of the magnetic Freedericksz transition should occur.

The thresholds of the magnetic Freedericksz transition of the liquid crystal (B_C) and the ferronematic (B_{CFN}) were estimated as the magnetic field where the capacitance variation (indicating the distortion of the director) reached 10% of its maximum. Fig. 6 shows the obtained critical magnetic field values for the magnetic Freedericksz transitions in the pure 6CHBT as well as in 6CHBT doped with the magnetic nanoparticles of different size. In the case of sample M1 the size (4.2 nm) of the magnetic nanoparticles is below the Shliomis size (see size distribution in Fig. 1). Therefore upon application of an external magnetic field the magnetic moments undergo a Néel rotation.

Indeed, an increase of the critical magnetic field was observed, as expected. For sample M2 with mean size around the Shliomis size, due to the polydispersity of the particles (Fig. 2) in this case both Néel and Brownian rotations should be present in the sample. The fact that the sample doped with magnetic particles M2 has lower critical magnetic field that the pure 6CHBT indicates, however, a dominance of the Brownian rotation. For samples doped with magnetic particles with size 31.4 nm and 112.7 nm (which are much above the Shliomis size) further decrease of the critical magnetic field was observed, as expected since in both these cases the Brownian rotation is present.

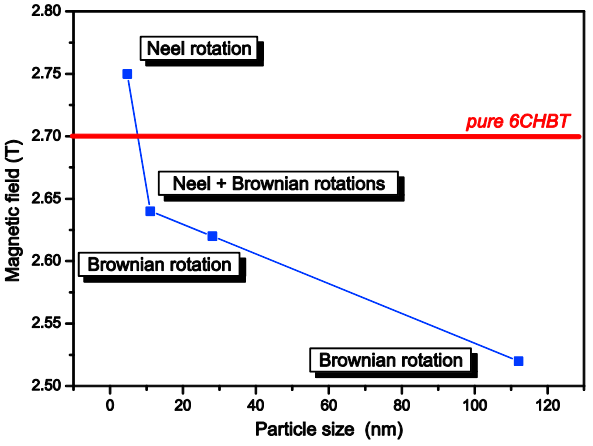

Figure 6: Dependence of the critical magnetic field on the size of magnetic particles

4. Conclusion

The influence of the size of the nearly spherical magnetic particles on the magnetic Freedericksz transition in 6CHBT-based ferronematics was studied. After doping the liquid crystal with the magnetic particles of smaller size than the Shliomis size, the increase of the critical magnetic field was observed, but after doping with the magnetic particles with larger size than the Shliomis size, the decrease of the critical magnetic field was observed. We can conclude that the size of the magnetic particles has an influence on the behaviour of the ferronematics in magnetic field.

Acknowledgement

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