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# Ferromagnetic nanoparticles suspensions in twisted nematic

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## HIGHLIGHTS

- A study of magnetic nanoparticles insertion in planar and twisted nematic cell was performed.
- A decrease of the Freedericksz transition threshold was observed in twisted cells.
- A theoretical model to explain decrease of Freedericksz transition threshold was developed.

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## ABSTRACT

Ferromagnetic nanoparticles insertions in nematic liquid crystals (NLC) in twisted configuration are studied and a theoretical model is proposed to explain the results. Experimental observation revealed that nanoparticles tend to overcrowd in long strings parallel to the rubbing direction of the alignment substrate of the LC cell. Their behavior under external field was studied and their interaction with their nematic host is described using elastic continuum theory.



## 1. Introduction

Nematic liquid crystals (NLC) represent an ideal medium for nanoparticle's study, due to their molecular order and their ability to connect to the surface. Thus, the particles are dispersed in an elastic and organized environment and their physical properties can be analyzed from the interaction forces with the NLC molecules. In addition, new nematic mixtures are obtained with controllable parameters based on nanoparticles concentration.

The original idea of yielding ferronematics belongs to Brochard and De Gennes [1] who proposed the doping of liquid crystals with small amount of fine magnetic nanoparticles (MNP-s) to enhance the sensitivity to magnetic fields since pure LC, because of their diamagnetic susceptibility small anisotropy, are characterized by relatively large range of structural transition threshold.

Ferrites are known as low cost materials provided with remarkable physical properties as well as chemical stability, thus being suitable for many application fields. When prepared as nanosized systems, they may have superparamagnetic features [2], gas sensing capability and catalytic activity [3] that recommend MNPs for magnetic data storage, sensors, transducers and actuators [4] and also for biomedical purposes (magnetic imaging, drug delivery, cancer hyperthermia) [5]. Further development of magnetic nanocomposites became one of the most attractive research areas in advanced materials [6].

Since they act completely different from macroscopic granules made of the same substance, there are many papers reporting new materials and devices based on such microparticles or nanoparticles [7–13]. In isotropic phase, nematic liquid crystals with ferromagnetic platelets act like a common ferrofluid [14] but in crystalline phase, a completely different behavior is observed due to the anchoring angle of the molecules on the particles surface and also to the interaction energy between the components of the system (molecule–molecule, molecule–nanoparticle or nanoparticle–nanoparticle). Using these mixtures, new phenomena were discovered and new methods were developed in order to obtain the best dispersion [15–17]. When subjected to an external magnetic field, nematic molecules tend to align themselves to the field direction if the intensity is higher than a critical value. This is called the magnetic Freedericksz transition and the threshold value ($B_c$) can be experimentally measured. Nanoparticles insertion in the nematic matrix has a significant influence on the critical field, depending not only on the nature of the liquid crystal but also on its orientation. An estimation of this field can be obtained

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from the experimental plot of the laser intensity versus the field induction but an exact value can be obtained using a theoretical method based on the continuum elastic medium similar to the one presented in [18].

## 2. Experimental set-up and measurements

Glass plates previously prepared for planar alignment were used for the LC cells. In order to obtain the planar alignment, a layer of 0.1% polyvinyl alcohol solution was spread by spin coating on the glass surface, then baked at 120 °C for 60 min, cooled at room temperature and rubbed with a smooth cloth to obtain the desired ditches direction. In order to obtain a low critical value we prepared thick cells by using thin glass slides (180 μm) as spacers. For the homogenous (planar) cell the ditches on the two plates are parallel to each other, while for the twisted one they are perpendicular to each other. Co-precipitation adapted method was applied to yield cobalt ferrite nanosized particles from iron chloride and cobalt sulfate at molar ratio 2:1, in alkali reaction medium (2 M NaOH) as described in detail in [19]. All reagents were pure Merck chemicals used without further purification while deionized water was provided by Barnstead EASYPureII ultrapure water system (18.2 MΩ/cm). After precipitated particle separation from the reaction medium they were repeatedly washed with deionized water to remove any other chemical traces; then perchloric acid aqueous solution (25%) was added to coat particle surface with perchlorate ions in order to ensure a uniform colloidal suspension by balancing magnetic attraction forces by means of electrostatic repulsion [20]. The witness cell was filled with 5CB nematic from Aldrich, while the test one was filled with a mixture of 5CB and 0.1% (volumetric fraction) of $CoFe_3O_4$ powder obtained by evaporation from a water based ferrofluid. Each sample was placed between the two hollowed poles of an electromagnet and a couple of crossed polarizers. The evolution of the emergent beam versus the field intensity was recorded and plotted on a computer (Fig. 1).

When the critical value for the magnetic Freedericksz transition is reached, the molecules tend to align themselves by the field direction. This leads to a decrease of the laser intensity which can be easily observed from the experimental plot. The molecular reorientation does not appear at once but after a time depending on elastic constants of the liquid crystalline mixtures and magnetic field. This is the reason why for each value of the applied field we waited for few minutes before the laser beam intensity was measured.

## 3. Results and discussions

In accordance with the theoretical model described in [21] the insertion of ferromagnetic nanoparticles in planar nematic LC cell leads to an increase of the critical threshold for the Freedericksz transition as it can be observed from the light intensity versus magnetic field plot presented in Fig. 2. Using the same substances in twisted cells, we notice that the critical threshold does not change for the 5CB sample (about 0.04 T) but in the case of the

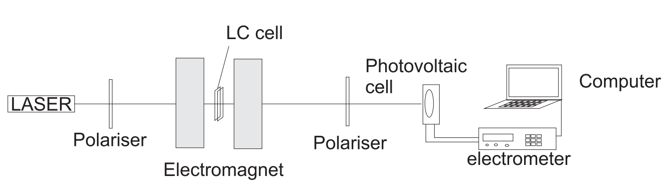


**Fig. 1.** Set up for experimental evaluation of critical field for magnetic Freedericksz transition.

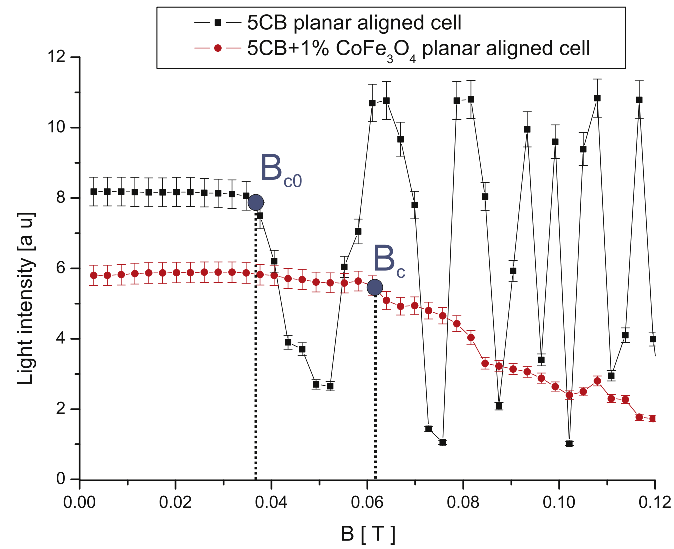


**Fig. 2.** Magnetic Freedericksz transition for planar cells. Square dots represent the plot for 5CB and disc circular dots represent the plot for 5CB + ferromagnetic particles mixture.

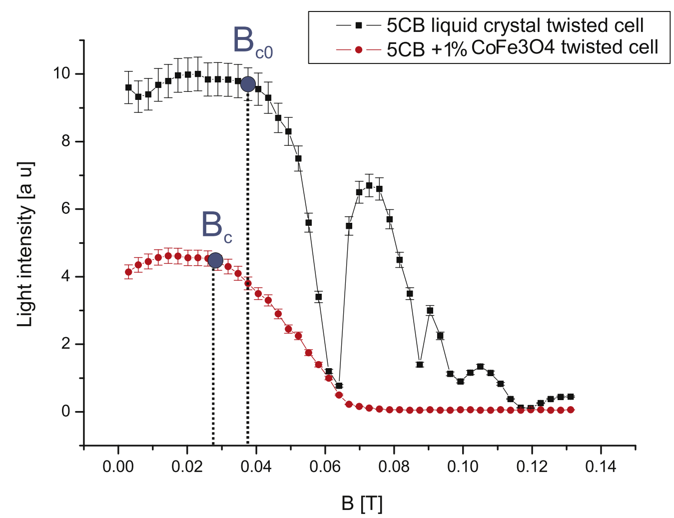


**Fig. 3.** Magnetic Freedericksz transition for twisted cells. Square dots represent the plot for 5CB and disc circular dots represent the plot for 5CB + ferromagnetic particles mixture.

5CB+1% $CoFe_3O_4$ filled cell it decreases down beyond 0.03 T, suggesting that the molecules align themselves easier with the field (Fig. 3). Nanoparticles size as given by SEM measurements is 40 nm, but after filling the aligned cells with the mixture we observed that the particles were gathering together in long chains just as presented in [22]. Length evaluation, made after the system stabilized itself, gave an average value of 2 μm (Fig. 4b, d). The clusters seem to be less agglomerated in the twisted cell due to the rotation of the distortion angle in consecutive layers. In contrast to planar aligned cell where parallel strings in the transparent layers give us the impression of very tight strings (Fig. 4b), in twisted cell we see a lattice made of strings in different planes (Fig. 4d). Besides, when the magnetic field is applied, a faster reorientation is observed. Experimental studies performed on other mixtures of liquid crystals and microparticles or nanoparticles indicate specific ordered structures [23,24] especially for long particles (chains, nanotubes) which align themselves parallel to nematic director [25,26]. Thus a twisted structure was designed in Fig. 5 for theoretical analysis. Similar structures were also observed in cholesteric liquid crystals [27] confirming our assumption and results.