Capacitance changes in ferronematic liquid crystals induced by low magnetic fields

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The response in capacitance to low external magnetic fields (up to 0.1 T) of suspensions of spherical magnetic nanoparticles, single-wall carbon nanotubes (SWCNT), SWCNT functionalized with carboxyl group (SWCNT-COOH), and SWCNT functionalized with Fe_3O_4 nanoparticles in a nematic liquid crystal has been studied experimentally. The volume concentration of nanoparticles was $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$. Independent of the type and the volume concentration of the nanoparticles, a linear response to low magnetic fields (far below the magnetic Fréederiksz transition threshold) has been observed, which is not present in the undoped nematic.

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I. INTRODUCTION

The orientational order of liquid crystals can be controlled by electric or magnetic fields due to the anisotropy of dielectric permittivity and diamagnetic susceptibility. In a restricted geometry (between parallel substrates) this effect is called the Fréedericksz transition. The classical Fréedericksz transition in pure nematics has been studied in detail both experimentally and theoretically [1]. The relatively large anisotropy of the dielectric permittivity in usual nematics triggers the orientational response to an electric voltage already at a few volts. In contrast, because of the small value of the anisotropy of the diamagnetic susceptibility ($\chi_a \sim 10^{-7}$), magnetic fields H used for the same purpose have to reach rather large values ($B = \mu_0 H \sim 1$ T). In an 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 Gennes. They constructed a continuum theory of magnetic suspensions in nematic liquid crystals (ferronematics) in their fundamental paper [2], prior to the chemical synthesis of these systems. Many reports have shown that doping of liquid crystals with small amount of magnetic nanoparticles can lead to the decrease as well as to the increase of the threshold B_F of the magnetic Fréedericksz transition [3–7], depending on the anisotropy of diamagnetic susceptibility χ_a of the nematic host, and on the initial mutual orientation of the nematic director **n** and the magnetic moment **m** of the magnetic particles. For example, when $\chi_a > 0$ and $\mathbf{m} \parallel \mathbf{n}$, doping with magnetic nanoparticles decreases B_F [3,4], while in case of combination $\chi_a < 0$ and $\mathbf{m} \parallel \mathbf{n}$ [7], or that of $\chi_a > 0$ and $\mathbf{m} \perp \mathbf{n}$ [8], doping with the nanoparticles increases B_F.

In recent works by Podoliak *et al.* [9] and Buluy *et al.* [10] 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 (which finally leads to a Fréedericksz transition). The authors have measured an additional, linear response in ferronematics at low magnetic fields (far below B_F). In their analysis a theoretical model based on the Burylov-Raikher theory [11,12] has been presented. We have to note here that in Refs. [9,10] a weak bias magnetic field ($B_{\text{bias}} \approx 2$ mT) has also been applied parallel to **n** in order to align the magnetic dipole moments of the nanoparticles parallel with **n** as an initial condition. These recent works have inspired us to get more insights by approaching the phenomenon from a different experimental aspect: to perform *capacitance measurements* on the nematic liquid crystal 6CHBT doped with spherical magnetic nanoparticles, single-wall carbon nanotubes (SWCNT), SWCNT functionalized with carboxyl groups (SWCNT-COOH), and SWCNT functionalized with Fe_3O_4 nanoparticles (SWCNT/Fe_3O_4), however, without an aligning bias magnetic field ($B_{\text{bias}} = 0$).

II. EXPERIMENTAL

The synthesis of the spherical magnetic nanoparticles was based on co-precipitation of Fe^{2+} and Fe^{3+} salts by NH_4OH at 60 °C [4]. The size and morphology of the particles were determined by transmission electron microscopy (TEM). The mean diameter of the obtained spherical magnetic nanoparticles was 11.6 nm. SWCNT and SWCNT-COOH (produced by catalytic chemical vapor deposition technique) were purchased from Cheap Tubes Inc., and then functionalized with Fe_3O_4 nanoparticles. The synthetic route of the functionalization is described in details in Ref. [13], and the final SWCNT/Fe_3O_4 product is shown schematically in Fig. 1. SWCNTs (of mixed chirality) exhibit in about 60% semiconducting property and in about 40% metallic one. The length of nanotubes ranged from 0.5 to 2 μm, their outer diameter from 1 to 2 nm, and inner diameter 0.8–1.6 nm. The magnetic properties of all prepared nanoparticles were investigated by SQUID magnetometer (Quantum Design MPMS 5XL). The ferronematic samples were based on the thermotropic nematic 4-(trans-4′-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT), which was synthetized and purified at the Institute of Chemistry, Military Technical University, Warsaw, Poland. 6CHBT is a

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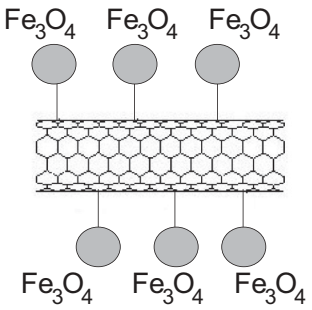

FIG. 1. (Color online) Schematic picture of the SWCNT functionalized with Fe_3O_4 nanoparticles (SWCNT/Fe_3O_4).

low-temperature-melting enantiotropic liquid crystal with high chemical stability [14]. The phase transition temperature from the isotropic liquid to the nematic phase has been found to be 42.6 °C. The heptan-based dispersion of spherical magnetic nanoparticles was added to the liquid crystal in the isotropic state under stirring until the solvent has evaporated. The doping with nanotubes was done by adding particles under continuous stirring to the liquid crystal in the isotropic phase. The volume concentrations of the nanoparticles were $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$, i.e., small enough to keep the interparticle magnetic dipole-dipole interaction ignorably small [12].

Structural transitions in ferronematic samples have been monitored by capacitance measurements in a capacitor made of indium-tin-oxide (ITO) coated glass electrodes. The capacitor with the electrode area of approximately (1×1) cm^2 has been connected to a regulated thermostat system, with a temperature stability of 0.05 °C. Measurements were performed at the temperature of 35 °C. The distance between the electrodes (the sample thickness) was $D = 5$ μm. The capacitance was measured at the frequency of 1 kHz and voltage of 0.1 V by a high-precision capacitance bridge Andeen Hagerling. In the experiments, the liquid crystal had planar alignment. The planar alignment was achieved by polyimide layers rubbed antiparallel, which produces a small pretilt θ_0 typically between 1° and 3°; see, e.g., Ref. [15]. The capacitance of the cells had a value C_0 for this alignment. The magnetic field was applied perpendicular to the electrode surfaces (as shown in Fig. 2). The measurements were done immediately after the cells were filled.

III. RESULTS

In the pure 6CHBT the magnetic Fréedericksz transition starts at 2.63 T. Due to doping, the Fréedericksz threshold is shifted to lower values [4,13], but it is still higher than 2 T.

Figures 3, 4, 5, and 6 show the relative capacitance variation $\frac{C-C_0}{C_0}$ of the 6CHBT liquid crystal doped with spherical magnetic nanoparticles, SWCNT, SWCNT-COOH,

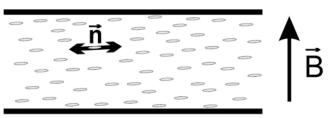

FIG. 2. Cross section of the cell in the initial state, which also demonstrates a small (≈3°) pretilt θ_0.

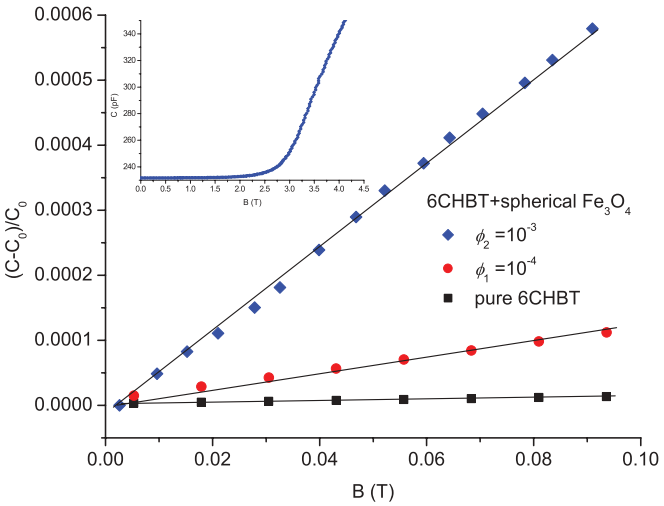

FIG. 3. (Color online) Relative capacitance variation vs magnetic field for 6CHBT doped with spherical Fe_3O_4 nanoparticles. The inset shows the magnetic Fréedericksz transition for the sample doped with magnetic particles of volume concentration ϕ_2. Symbols are the experimental data, and the lines represent linear fit to them.

and SWCNT/Fe_3O_4, respectively, as a function of the magnetic induction B in the low magnetic field range (up to 0.1 T), far below the threshold of the magnetic Fréedericksz transition. The figures provide a clear evidence for a linear magnetic field dependence of the *capacitance* in this low magnetic field region, i.e., for the presence of an effect similar to that obtained by an *optical* method as reported in Refs. [9,10]. The magnetic field dependence of $\frac{C-C_0}{C_0}$ is stronger for a higher volume concentration of nanoparticles in all cases, but it is not present in the undoped liquid crystal. The sensitivity of the suspensions to the field depends on the type of the nanoparticle used. The lowest response was detected for doping with SWCNT-COOH, while a much larger response was measured for doping with spherical magnetic particles Fe_3O_4 and SWCNT/Fe_3O_4. Even the nematic suspension

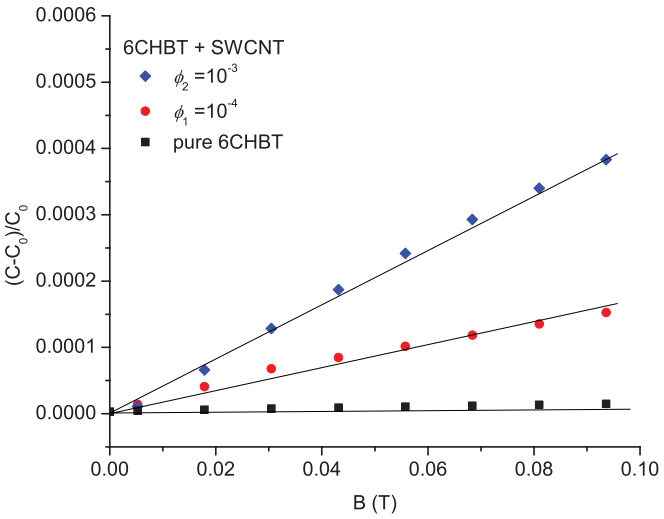

FIG. 4. (Color online) Relative capacitance variation vs magnetic field for 6CHBT doped with SWCNT. Symbols are the experimental data, and the lines represent linear fit to them.

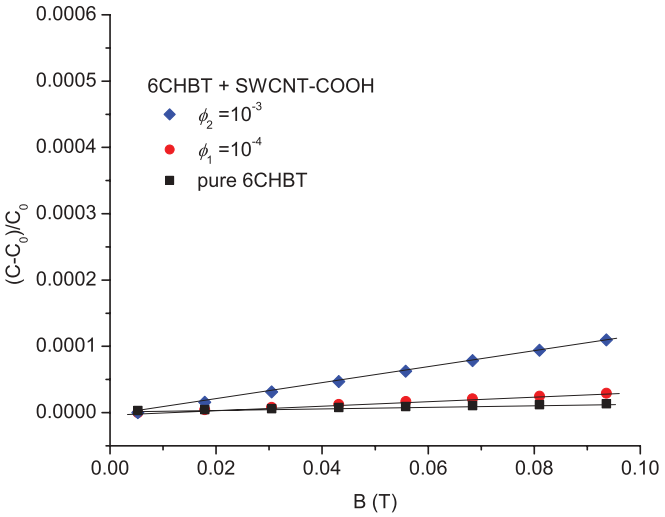

FIG. 5. (Color online) Relative capacitance variation vs magnetic field for 6CHBT doped with SWCNT-COOH. Symbols are the experimental data, and the lines represent linear fit to them.

with the net SWCNT showed a considerably larger effect than that with SWCNT-COOH. Note that for the suspension with the larger SWCNT/Fe_3O_4 concentration ($\phi_2 = 10^{-3}$) a different (nonlinear) magnetic field dependence of the reduced capacitance is detected. A qualitatively similar low magnetic field effect has been measured optically in nematic colloids of carbon nanotubes filled with α-Fe, in which a strong aggregation has been observed on the time scale of hours [9].

IV. CONCLUSIONS

The data shown above confirm that ferronematic suspensions may show well measurable response in capacitance to the magnetic field even much below the classical magnetic Fréedericksz threshold. Our experimental results, on the one hand, are in agreement with the recent reports [9,10], regarding the dependence of the effect on the concentration and type of

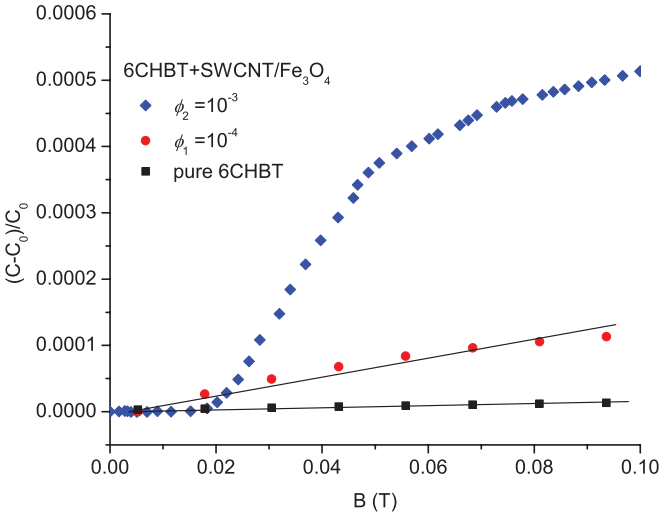

FIG. 6. (Color online) Relative capacitance variation vs magnetic field for 6CHBT doped with SWCNT/Fe_3O_4. Symbols are the experimental data, and the lines represent linear fit to them.

nanoparticles. On the other hand, our measurements indicate that the aligning bias magnetic field (used in Refs. [9,10]) is not an essential prerequisite for the nematic suspensions to be sensitive to low magnetic fields. The possible reason for this deviation regarding B_{bias} is that the ferronematics were based on different nematic hosts in these experiments. In Ref. [10] the 4-cyano-(4′-pentyl)biphenyl (5CB) has been used, while in Ref. [9] the mixture E7 served as a host, which is also composed of various cyanobiphenyls. For the compound 8CB (which belongs to the same family) it was shown [16] that it prefers a perpendicular initial alignment ($\mathbf{n} \perp \mathbf{m}$) between the director $\mathbf{n}$ and the magnetic moment $\mathbf{m}$ of the nanoparticle. The role of the bias magnetic field could be to overwrite this initial condition yielding $\mathbf{n} \parallel \mathbf{m}$. In the 6CHBT-based ferronematics used by us, however, $\mathbf{n} \parallel \mathbf{m}$ is the preferred initial condition (even in the absence of a bias field) [16].

A much more challenging task is to interpret the detected linear response in capacitance to low magnetic fields. The continuum theory allows the possibility for such a linear coupling only in the presence of both the nonzero initial pretilt θ_0 and the magnetic dipole moment $\mathbf{m}$ of the nanoparticles. Namely, without pretilt, in the limit of small changes, the dielectric permittivity (and by that, the capacitance) depends only quadratically on the change in the director out-of-plane tilt $\Delta\theta$. However, when a pretilt is present, a linear term $\theta_0\Delta\theta$ will also enter the expression for the permittivity. On the other hand, the free energy of the system (which has to be minimized to obtain a solution) will contain a term linear on the magnetic field only if the magnetic moment of the magnetic particles $\mathbf{m}$ is taken into account through the dipolar interaction between the particles and the magnetic field; see Eq. (2) of Ref. [9]. The proper combination of these effects of θ_0 and $\mathbf{m}$ may eventually lead to a solution showing the experimentally observed linear C(B) dependence. Therefore, in this regard further theoretical and experimental investigations are desirable, primarily concentrating on the role of the pretilt θ_0. Theoretically the introduction of θ_0 into the Burylov-Raikher theory, while experimentally a systematic variation of the pretilt (by different surface treatments) could serve as the first step forward.

Interestingly, 6CHBT doped with "nonmagnetic" SWCNT (Fig. 4) has a comparable low magnetic field response to those ferronematics obtained by doping 6CHBT with magnetic particles (spherical, Fig. 3, and SWCNT/Fe_3O_4, Fig. 6), while in 6CHBT doped with SWCNT-COOH the detected response is considerably lower (though still nonzero; see Fig. 5). These observations lead to two main conclusions. First, both "nonmagnetic" SWCNTs and SWCNT-COOH particles have a nonzero magnetization. This has actually been measured for our SWCNT [13] and is also supported by both theoretical and experimental investigations performed on carbon nanotubes, which have shown that nanotubes may have diamagnetic as well as paramagnetic properties depending primarily on their electronic structure (see, e.g., Refs. [17–21]). Second, the functionalization (either with COOH or with Fe_3O_4) of the carbon nanotubes (which are of mixed chirality, and exhibit both semiconducting and metallic properties) leads to further complications. Namely, the functionalization alters also the interaction between the particles and the liquid crystal (i.e., the anchoring energies are different). Therefore, magnetic

properties of the given SWCNT, as well as the type of the anchoring, and the magnitude of the anchoring energy has to be taken into account to interpret these results in a proper way.

The results and conclusions presented above imply that a deeper, more detailed analysis of the theoretical model [9,10], focusing on the low magnetic field limit is necessary for the interpretation of the low field response (both optical and capacitive) of ferronematic suspensions. This statement is also supported by the optical results of Ref. [9] for higher concentrations ($\phi \geqslant 10^{-4}$) of nanoparticles, where only a moderate agreement between the model and the experimental curves has been achieved.

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