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Magnetic behavior of 10 nm-magnetite particles diluted in lyotropic liquid crystals

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A magnetic study of 10 nm magnetite nanoparticles diluted in lyotropic liquid crystal and common liquids was carried out. In the liquid crystal the ZFC-FC curves showed a clear irreversible behavior, and it was possible to distinguish the nematic from the isotropic phase since the magnetization followed the dependence of the nematic order parameter with the temperature. This behavior could be mimicked by Monte Carlo simulation. © 2011 American Institute of Physics. [doi:10.1063/1.3549616]

I. INTRODUCTION

The study of systems formed by magnetic nanoparticles (NPs) has attracted a great amount of interest due to the large variety of applications in technological and biological areas. It is sometimes difficult to determine which of the most relevant microscopic effects (surface magnetic disorder, dipolar interactions, and interaction between surface moments and the particle’s neighborhood) are those that determine the macroscopic behavior of a system of nanoparticles. The hallmark of the magnetic nanoparticle’s behavior is its superparamagnetism at room temperature. This restricts the use of such systems in, for example, magnetic recording and hyperthermia. So, research to find new mechanisms that are able to harden the particle surface and raise their blocking temperature is a major goal. There are experimental results that show changes in the saturation magnetization in magnetite-based nanoparticles using different coupling agents on the particle’s surface. Another interesting result is the expressive increase of coercivity of CoFe$_2$O$_4$ nanoparticles diluted in polymeric liquid crystal.

Systems formed by magnetic particles and liquid crystals (ferrolyotropics) have been studied for several decades. In a lyotropic liquid crystal the nematic phase is characterized by the presence of anisotropic micelles that show spatial ordering and an anisotropic optical axis, while the isotropic phase shows more spherical micelles. Liquid crystals have a preferred direction-dependent phase (director) that can be oriented in a magnetic field on the order of 10,000 Oe, due to the diamagnetic character of the material. In Ref. 9 the authors proposed the theory that doping nematic liquid crystal with anisotropic needle-shaped magnetic particles (∼100 nm) could reduce that magnetic field to roughly 100 Oe. That result was achieved theoretically by considering a mechanical coupling between the nematic phase director and the anisotropic magnetic grain. Experiments showed that nearly spherical ferromagnetic particles with diameters around 10 nm can reorient the liquid-crystalline matrix in fields as low as 10 Oe. It is noteworthy that magnetite nanoparticles of about 10 nm in an aqueous solution are superparamagnetic at room temperature but they display magnetic irreversible behaviors when mixed in the liquid crystal. The mechanism leading to this apparent magnetic hardening of the nanoparticles is not yet well understood, and the few works that do focus on this problem are inconclusive.12,13

In this work, we present a study on the magnetic behavior of magnetite (Fe$_3$O$_4$) nanoparticles diluted in: a) water, b) a binary isotropic mixture of water and potassium laurate, and c) a lyotropic liquid crystal. Measurements of zero field cooling and field cooling (ZFC-FC) and ac susceptibility were carried out. Monte Carlo simulations were performed in order to interpret the experimental results.

II. EXPERIMENTAL METHODS

Potassium laurate (LK) soap was utilized to prepare the lyotropic liquid crystal samples. Two kinds of liquid crystal samples were prepared: Binary, a mixture of water and LK, and ternary, composed of water, LK, and decanol (DeOH). Table I shows the composition of the liquid crystals, water, and water with LK (below the critical micellar concentration) samples. All of them were doped with the EMG605 ferrofluid from Ferrotech Co., which consists of a mixture of 10 nm cationic magnetite nanoparticles dispersed in water. Table I also shows concentrations of magnetic particles per volume of sample.

The magnetic characterization of the samples was obtained by ZFC-FC curves with 50 Oe applied field and ac magnetic susceptibility between 0.1 and 100 Hz, both measured in a superconducting quantum interference device magnetometer (Quantum Design). The temperature range of the measurements was between 283–350 K in order to prevent the freezing and evaporation of the samples, that were measured inside a quartz cylinder with an internal diameter of 3 mm and 2 cm of height.

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III. RESULTS AND DISCUSSION

Figure 1 compares the magnetic behavior of approximately identical magnetite nanoparticles diluted in three different liquids: water (sample FFW), an isotropic mixture of LK and water with LK concentration low enough to not form micelles (sample I1), and an isotropic mixture of LK and water with LK concentration sufficient to form micelles (sample I2). Interestingly, the only sample where the magnetite nanoparticles show magnetic irreversible behavior (since the ZFC and FC curves are not overlapping) is the sample where the environment of the particles is an aggregate of micelles (I2). The magnetization of sample I2 display a clear irreversibility below $T_I = 317(2)$ K, since when the temperature is higher than $T_I$ the curves ZFC and FC are coincident within the experimental inaccuracy, whereas for temperatures smaller than $T_I$ the ZFC and FC curves become distinct. It is more clearly shown in the inset of Fig. 1, where the difference $M = M_{FC} - M_{ZFC}$ was plotted as a function of the temperature for samples I1 and I2.

Figure 2 shows the ZFC-FC and ac susceptibility curves of magnetite nanoparticles diluted in the fourth liquid under test: A ternary mixture of water, LK, and decanol (sample N1). Both I2 and N1 are lyotropic liquid crystals (i.e., both are micellar). However, while I2 is micellar isotropic throughout the range of temperatures studied, N1 is micellar discotic (micelles with disk shape) only between 286(1) and 312(1) K, as determined by optical measurements. Below 286 K and above 312 K, N1 is micellar isotropic. These phase transitions (isotropic-discotic at 286 K and discotic-isotropic at 312 K) are characteristic of this liquid crystal and their transition temperatures are not changed significantly by the presence of magnetic nanoparticles (at least at the low concentrations used here). Figure 2 clearly shows irreversible magnetic behavior of magnetite nanoparticles diluted in the liquid crystal micellar. This is concomitant with that observed for sample I2, but in this case and given the highest concentration of LK, if there is a $T_I$, it exceeds the maximum measured in our study. Conversely, as a notable feature in this figure, it is evident that the measurement of magnetization of the nanoparticles can be used to determine the phase transitions of liquid crystal. Furthermore, between 286–312 K we see that the magnetization has a bell-shaped behavior that is characteristic of the variation of the order parameter $S$ with the temperature in the nematic discotic phase. The ac susceptibility curves (inset of Fig. 2) present a discontinuity at the same temperatures observed for the ZFC-FC measurements and the frequency dependence is characteristic of magnetic irreversibility.

The interesting question is why the magnetization follows the behavior of the order parameter of the liquid crystal. The explanation of this fact is that the nanoparticles are anchored to micelles and follow their movement, so the magnetization is sensitive to the orientational order of the liquid crystal. In the discotic phase the micelles have the shape of disks and when the order parameter $S$ is maximum, the micelle’s shape anisotropy is maximum too, with the direction of symmetry perpendicular to the plane of the micelles and to the applied field. Near the temperatures of phase transition the micelles are more spherical, so there is less ordering and $S$ has a lower magnitude. So if the magnetic particles are confined between the micelles and follow their orientation the magnetization will have the same qualitative behavior as $S$.
IV. MONTE CARLO SIMULATION

The experimental ZFC-FC curves presented in the previous sections show two main results for the magnetization behavior: irreversibility at room temperature and a bell-shape typical of the dependence of discotic order parameter on the temperature. Those effects occur concomitantly for discotic samples, but may have different origins. We implemented Monte Carlo simulations using the Metropolis algorithm in order to acquire a better understanding of our experimental results.

The simulated system was an ensemble of 360 noninteracting spherical particles, where each particle was formed by 1180 magnetic moments distributed in a simple cubic lattice. The magnitude of each vector \( \mu_i \) is the value of the magnetic moment for one magnetite unit cell, whose value is 4.1 \( \mu_B \).

Equation (1) shows the energy for each magnetic moment, following the Heisenberg classical model. The energy terms considered were Zeeman, uniaxial magneto-crystalline, and exchange between the first neighbors \( j \).

\[
E_i = -\mu_i \tilde{h} \sum_{(j)} J \cos \theta_{ij} + K_1 V \sin^2 \theta_i, \tag{1}
\]

Our experimental results show that the nanoparticles are sensitive to changes in the liquid crystal order in a way that, when the liquid crystal order is maximum, the magnetization is also maximum. We can conclude that the liquid crystal order favors the alignment of the nanoparticles with the applied magnetic field. This effect can be expressed in terms of the angle \( \theta \) between the easy axis of the nanoparticles and the field direction. We can consider that the isotropic phase does not impose any restriction in the values that \( \theta \) can assume, with the easy axis of the 360 particles distributed isotropically, while the nematic phase does.

\[
S = 0.5 < 3 \cos^2 \theta - 1 >. \tag{2}
\]

From our experimental data from the N1 sample, the isotropic-nematic and nematic-isotropic phase transitions occur at 290 and 312 K, respectively. In this temperature range the \( \theta \) angle of each particle is chosen using a Gaussian random number generator, in which the average \( \theta \) for the Gaussian distribution is extracted from Eq. (2). We can approximate the dependence of \( S \) on the temperature by a parabola with maximum value \( S = 1 \) at 301 K and values \( S = 0.5 \) for 290 and 312 K looking for \( \theta \) values between 0 and \( \pi \) that satisfies Eq. (2). Figure 3 shows the average FC obtained from 25 Monte Carlo simulations for 360 particles with \( J = 2.3 \times 10^{-21} J \). Figure 3 shows only the curve FC, due to the fact that since the ZFC curve is a metastable state, it can be changed simply by altering the conditions of the simulation (such as the initial state) to mimic the irreversibility. As we can see, the simulation can describe the quantitative behavior of the magnetization quite well when the liquid crystal is in the nematic phase.

V. CONCLUSION

The magnetite nanoparticles showed an irreversible behavior at room temperature when diluted in lyotropic liquid crystal, different from that observed for common liquids and nonmicellar mixtures. The magnetization follows the dependence of the discotic order parameter with the temperature and this behavior could be accounted for by a mechanical coupling between micelles and NPs, as shown by Monte Carlo simulations.