1 Introduction

Liquid crystal (LC) research was predominantly boosted in 1970s by the liquid crystal display (LCD) technology, and primarily focused on the design, synthesis and characterization of the LC materials, as well as on the development of new LCD modes, in order to fulfill the requirements of the newborn, rapidly expanding LCD industry. Now, the commercial success of the LCDs has moved the research and development in this field mostly into industrial laboratories. In the meantime, the academic LC research has been shifted towards the search for novel smart functional materials applicable in other diverse fields such as micro-, nano-, and biotechnology, medicine, polymer and colloid science, photonics, etc.

In this respect, the research of LC colloidal systems (various micro-, or nanoparticles dispersed in LCs) offer a wide range of possibilities. The use of nematic LCs as the colloidal matrix is especially of great promise, primarily because nematics provide possibilities. The use of nematic LCs as the colloidal matrix is especially of great promise, primarily because nematics provide a unique opportunity to generate, transform, and control topological defect (TD) structures (point, line, or sheet disclinations). TDs in general strongly interact with the embedded micro-, or nanoparticles (which, again generate TDs around themselves when dispersed in a LC matrix), and that can be exploited for efficient trapping and control of the particles. The TD mediated self-assembly of particles offers possible applications in photonics (e.g. 3D photonic crystals, and metamaterials), while the control of TDs may be used, e.g. for the guided transport of microfluidic cargo.

Magnetic nanoparticles (MNPs) dispersed in nematic LCs – the so called ferronematics (FNs) – are the practical manifestation of the idea proposed by Brochard and de Gennes who suggested that doping liquid crystals with fine magnetic particles, even in a very low concentration, might significantly enhance their response to magnetic fields. After the first implementation of ferronematics, numerous experimental works have been done on FNs, which relate to, but are not limited to: the response of FNs to low magnetic fields, the magnetic field induced shift of the phase transition temperature, the shear flow in FNs, and the dynamics of FNs in a magnetic field. Results of all these efforts evidence that doping the nematic matrices with a small amount of MNPs affects the properties of the composite materials considerably, and therefore, nowadays FNs in the form of stable nematogenic magnetic suspensions are considered as promising materials due to their high magnetic sensitivity resulting from a subtle orientational coupling between the ferromagnetic nanoparticles and mesogenic molecules.

However, to the best of our knowledge, studies on the basic magnetic, especially magnetodynamic properties of FNs are rather scarce. To advance this area, here we investigate the magnetic susceptibility of FNs in response to a probing alternating magnetic field. We find an unusual behaviour of the magnetic susceptibility while passing through the phase transition of the FN, sensing the prior presence of a small (few Oe) magnetic field. We also provide a possible phenomenological explanation of the experimental results, which is related to defect-mediated aggregation of MNPs.
2 Experimental

Measurements were performed on a FN sample based on the calamitic thermotropic liquid crystal \( n \)-hexylcyanobiphenyl (6CB).\(^{25,26} \) The temperature \( T_{I-N} \) of the isotropic (I) to nematic (N) phase transition of neat 6CB is 302 K. The liquid-crystalline matrix was doped with spherical grains of \( \text{Fe}_3\text{O}_4 \) (magnetite) particles.

Fig. 1 shows a transmission electron microscopic (TEM) image, and the size distribution of the magnetic particles. The mean diameter of MNPs is \( d = 20 \) nm with a half-width of the size distribution of only \( \pm 2 \) nm, \( i.e. \), the particles are quite monodispersed. This is important considering the findings that the polydispersity of MNPs promotes their aggregation in colloidal systems.\(^{27} \)

Prior to the dispersion in the LC matrix, MNPs were coated with oleic acid (providing an appropriate strong interaction of mesogenic molecules with the surface of the nanoparticles, thus detaining the aggregation of MNPs) and dissolved in chloroform. This solution was admixed to the liquid crystal in its isotropic phase, and then the solvent was allowed to evaporate during an ultrasonification process. The procedure resulted in a FN, with a volume concentration of the MNPs of \( \phi = 10^{-4} \). This composition of the FN turned out to be very stable: no micron-sized aggregates could be found more than three years after the preparation (in contrast to some other FNs, where aggregates of several tens of micrometer were found within few months after the preparation\(^{28} \)). We associate this stability with the monodispersity of the MNPs, with their relatively small size, with their low volume fraction, and with the subtle interaction between the oleic-acid-layer-covered MNPs with the given LC matrix, altogether.

For magnetic measurements, both the neat and the doped 6CB were put into cylindrical capsules, 2.5 mm in diameter and 6.5 mm in length. The magnetic properties were measured with a SQUID magnetometer (Quantum Design MPMS 5XL) in a magnetic field directed along the cylindrical axis of the capsules.

3 Results and discussion

In Fig. 2 the magnetization curves of both the undoped (neat) and doped 6CB are presented in the nematic phase (at \( T = 290 \) K) and, additionally, for the doped sample in the isotropic phase (at \( T = 320 \) K). The neat 6CB exhibits usual diamagnetic behavior, while the FN composite at low magnetic fields behaves as a superparamagnet displaying no hysteresis. The diamagnetic features of the host matrix become dominating only at higher magnetic fields. The shape of the magnetization curves of the doped sample is the same in both the isotropic and nematic phases, indicating that the quasi-static magnetic properties are independent of the type of the fluid phase of the host material.

The dynamic susceptibility \( \chi \) of the prepared samples is measured in the same experimental geometry. An ac magnetic field of 1 Oe is applied at the frequency of \( f = 650 \) Hz. To measure the temperature dependence of \( \chi \), the samples are first heated to 320 K (isotropic phase) and then slowly cooled down (with the rate of 0.5 K min\(^{-1} \)) to the nematic phase; after that they are slowly heated up again to 320 K. The sample is thermally stabilized at each temperature for 3 min before performing the susceptibility measurement.

Fig. 3a shows the temperature dependence of the real component \( \chi' \) for both the undoped and doped 6CB. As it should be,
the ac susceptibility of the neat 6CB is small and negative. In contrast to that, the response of the FN sample is positive and much higher than that of the undoped 6CB, in agreement with the magnetization curves shown in Fig. 2. Notably, for both samples the temperature dependence of $\chi'$ is rather weak. Moreover, no change is detected when passing through the I–N phase transition, either on cooling or on heating. The susceptibility values,

$$\chi'_{\text{I}} \simeq \chi'_{\text{N}} \simeq 4.0 \times 10^{-6} \text{ emu}, \quad (1)$$

of the FN are well reproducible through several cooling–heating cycles (even on the time scale of years).

Fig. 3b shows the results of a similar experiment, except that prior to the same cooling–heating cycle, the samples were subjected to a dc magnetic field $H_{\text{dc}} = 20 \text{ kOe}$ in the isotropic phase, viz. at 320 K. In case of a neat 6CB, the magnetic field does not alter the temperature dependence: the curve in Fig. 3b replicates the one in Fig. 3a. A surprising fact, however, is that under this condition the ac susceptibility of the FN in the isotropic phase,

$$\chi'_{\text{I}} \simeq 4.4 \times 10^{-6} \text{ emu} \quad (2)$$

is higher than $\chi'$ in Fig. 3a. Moreover, on cooling, an abrupt change of $\chi'$ occurs at the temperature corresponding to the isotropic-to-nematic phase transition. Namely, $\chi'$ drops from $\chi'_{\text{I}}$ back to $\chi'_{\text{N}} \approx \chi'_{\text{I}}$. Upon heating, the ac susceptibility remains at that value, i.e., no change occurs on passing the N–I phase transition. During subsequent cooling–heating cycles (without application of a dc magnetic field), $\chi'$ remains unaltered. The higher $\chi'_{\text{I}}$ value could be restored, however, by re-applying $H_{\text{dc}}$ in the isotropic phase. We note that switching the $H_{\text{dc}}$ on and off in the nematic phase and then heating back to above $T_{\text{I–N}}$ does not affect the susceptibility of the ferronematic.

Fig. 4 shows $\chi'(T)$ under the same conditions as the experiment shown in Fig. 3b, except that the $H_{\text{dc}}$ values are lower. As Fig. 4a shows, the same higher value of isotropic ac susceptibility $\chi'_{\text{I}}$ and hence the jump

$$\Delta \chi' = \chi'_{\text{I}} - \chi'_{\text{I}} \approx 4.0 \times 10^{-7} \text{ emu} \quad (3)$$

at $T_{\text{I–N}}$ upon cooling may be induced by dc magnetic fields of different magnitudes. One finds that $\Delta \chi'$, ranging about 10% of $\chi'$, is independent of $H_{\text{dc}}$ in a wide range: $10 \text{ Oe} \leq H_{\text{dc}} \leq 20 \text{ kOe}$.
Fig. 4b evidences, however, that there exists a quite low “critical” value \( H_{dc} \approx 9 \) Oe, below which the induction effect disappears. From the above-presented observations we infer the following. First, a dc magnetic field applied in the isotropic phase alters the structure of the FN in such a way that its ac susceptibility increases. Second, the increase of the susceptibility is due to MNPs, since it is absent in the neat liquid crystal. Third, the magnetic field-induced structural changes that resulted in the increase of \( \Delta \gamma ' \), vanish when the composite enters the nematic phase. As a step towards understanding this behavior, let us estimate the main parameters which govern the response of the FN to the probing ac and bias dc magnetic fields.

The FN system in question is an ensemble of magnetic MNPs coated with oleic acid and suspended in the matrix of 6CB. For the estimations below we take the mean diameter of the particles as \( d = 20 \) nm, their volume concentration as \( w = 3.7 \) \( \times 10^{-4} \) emu/cm\(^3\) as in ref. 30. By relating the anisotropy energy of a particle, \( KV \), to the thermal energy \( k_B T \) (where \( V = \pi d^3/6 \) is the volume of a single MNP, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature), one has the nondimensional parameter

\[
\sigma = \frac{KV}{k_B T} \frac{\pi K d^3}{6k_B T} \approx 20. \tag{4}
\]

Such a value of \( \sigma \) evidences that the particles are virtually free of Néel superparamagnetism. In other words, each particle behaves as a nanosized permanent magnet, and its magnetic moment \( \mu \) is tightly bound to a certain internal axis. Thus, vector \( \mu \) cannot rotate in response to a magnetic excitation (ac field) except together with the particle body.

For a single-domain particle, the magnitude of its magnetic moment is defined as \( \mu = M_s V \), where \( M_s \) is the saturation magnetization of the ferromagnet. By setting for nanodispersed magnetite \( M_s = 400 \) emu cm\(^{-3}\) (see e.g. ref. 29), one obtains

\[
\mu = \frac{\pi M_s d^3}{6} \approx 1.6 \times 10^{-15} \text{ emu} \sim 1.7 \times 10^5 \cdot \mu_B. \tag{5}
\]

where \( \mu_B \) is the Bohr magneton.

The magnetic coupling of the particles is described by the pairwise dipole–dipole potential. The reference intensity of this interaction is given by the dimensionless parameter

\[
\lambda = \frac{\mu^2}{k_B T d^3} \approx 8. \tag{6}
\]

In view of the results of former studies on the aggregation effects in magnetic fluids, \(^31\) one concludes that this value is quite high. Therefore, in the situation under study, particle aggregation is highly probable. In other words, for such a system a thermodynamically stable state implies the presence of certain amount of multi-particle aggregates. This, in turn, means that even if in the initial state all the particles are positioned apart from one another, they tend to aggregate. This process might be rather slow but could be accelerated if the interparticle interaction is enhanced by aligning the magnetic moments with an external magnetic field. As the considered ensemble is rather dilute, when undergoing aggregation from the state of isolated particles, the most probable entities to emerge are pair aggregates (“dimers”). \(^29,32\)

The theoretical estimates for the magnetization curve in the isotropic phase of the system are as follows. The magnetization \( M \) of a dilute ensemble of isolated particles suspended in a fluid is

\[
M(H) = \phi M_s L(\xi), \quad \xi = \mu H/k_B T, \tag{7}
\]

where \( L(\xi) = \coth \xi - 1/\xi \) is the Langevin function, and \( \xi \) is the Langevin argument which relates the Zeeman energy (the energy of interaction of the particle’s magnetic moment with the applied field) to the thermal energy.

The static (equilibrium) initial susceptibility \( \chi_0 \) of the system that describes the initial slope of the magnetization curve is defined as

\[
\chi_0 = \frac{M(H)}{H} \quad \text{in the limit } H \to 0. \tag{8}
\]

As the Langevin function scales at \( \xi \to 0 \) as \( L(\xi) \approx \xi/3 \), one has: \(^{33}\)

\[
\chi_0 = \frac{\phi M_s^2 V}{3k_B T} \approx 5 \times 10^{-4} \text{ emu}. \tag{9}
\]

In the experiments, the limit \( \xi \to 0 \) is often not accessible, e.g. when recording the magnetization curve shown in Fig. 2, the lowest magnetic field was 50 Oe, since SQUID is not reliable below that value. Given that, we use \( \chi_{50} = M(H)/H \) measured at \( H = 50 \) Oe to approximate the static susceptibility. Keeping in mind that for our system this magnetic field amounts to \( \xi \approx 2 \), the function \( L(\xi) \), although being far from saturation, displays pronounced nonlinearity. Thus we surmise that the true \( \chi_0 \) is about 20% higher than \( \chi_{50} \).

Evaluation of the data shown in Fig. 2 sets the experimental value to

\[
\chi_{50} \approx 3.7 \times 10^{-6} \text{ emu}, \quad \text{that implies } \chi_0 \approx 4.6 \times 10^{-6} \text{ emu}. \tag{10}
\]

This value turns out to be about 100 times lower than the estimation in eqn (9). One cause of this discrepancy could be that the actual volume concentration of magnetite in the ferroemamatic is much lower than the nominal one determined from the synthesis conditions. Another, and in our view more relevant, cause is that the model of well-dispersed, isolated MNPs [used in deriving eqn (9)] fails for real samples. As noted above, the interparticle interactions are strong enough to provoke aggregation – see eqn (6), i.e. formation of multi-particle clusters. In the initial field-free isotropic state, such clusters are assumed to take configurations where the magnetic flux is nearly closed. Due to that, their effective magnetic moments are much smaller than the sum of those for the same
number of single particles. As a result, the contribution of multi-particle clusters to the magnetic susceptibility is quite low, except for the case of strong magnetic fields, which are not attainable in dynamic measurements.

Dealing with the dynamic susceptibility requires the analysis of its frequency dispersion properties. From general considerations, one infers that under a weak ac magnetic field only overdamped, i.e. forced oscillations are possible, which are rendered by a Debye-type formula

\[
\chi(\omega) = \frac{\gamma_0}{1 - i \omega \tau} = \chi' + i \chi'', \quad \chi'(\omega) = \frac{\gamma_0}{1 + \omega^2 \tau^2}, \tag{11}
\]

where \(\omega = 2\pi f\) and \(\tau\) is the characteristic response time. Eqn (11) shows that the maximum of the dissipation occurs at the excitation frequency \(f^* = \frac{1}{\tau}\). In the range \(f > f^*\) the ac susceptibility becomes considerably smaller than the static one (\(\chi' \ll \gamma_0\)), while for \(f < f^*\) one has \(\chi' \approx \gamma_0\).

The experiments presented in Fig. 3 and 4 are performed at the frequency of \(f = 650\) Hz. Fig. 5 shows the temperature dependence of \(\chi'\) measured under the same conditions, but at various (lower) exciting frequencies. From Fig. 3b, 4a and 5 it is seen that the susceptibilities \(\chi'_I, \chi'_{fI}, \chi'_{fN}\) and, thus, the magnitude of the jump \(\Delta \chi'\) at the I–N phase transition are practically independent of the frequency within almost 3 decades. From this observation one concludes that, on the one hand, the observed jump in \(\chi'\) is not due to the frequency dispersion and, on the other hand, the characteristic time of the system is \(\tau \approx 2.5 \times 10^{-4}\) s.

In the adopted model considering the dynamic susceptibility, the characteristic time of the system under weak ac excitation should be taken as the Brownian rotational diffusion time \(\tau_R = 3\eta V/kT\) of a spherical MNP of volume \(V\) suspended in a fluid with the dynamic viscosity \(\eta\). Upon entering the nematic phase, the viscosity of the matrix changes and becomes anisotropic; moreover, elastic torques acting on the particle emerge as well. Therefore, one anticipates a change of the characteristic time \(\tau\) of the system below \(T_{f-N}\). However, the above-presented experimental results evidence that \(\tau\), despite its changes at the phase transition, remains small enough not to induce dispersion in the studied frequency range. Therefore, one concludes that the behavior of \(\tau\) cannot be responsible for the jump in \(\chi'\) at \(T_{f-N}\).

The lack of dispersion implies that the measured dynamic susceptibility does not differ much from the quasi-static one. Comparison of \(\chi'_I\) in eqn (2) with the actual static susceptibility obtained from magnetization measurements, see eqn (10), confirms this inference.

In summary of the afore-presented experimental results, one can conclude that a weak dc magnetic field induces an enhancement of the ac susceptibility of a FN, an effect which disappears when passing through the I–N phase transition. We propose a possible phenomenological explanation for the occurrence of the observed effect, which is associated with the details of aggregation of MNPs in a nematogenic matrix. Proceeding the explanation, we note that in the isotropic phase of FN, the nanoparticles are presumably not ideally dispersed in the host liquid. As a consequence of eqn (6), single particles, if they are located close enough, attract each other and strive to form units of two MNPs (dimers), three MNPs (trimers), or sub-micron sized multi-particle clusters of MNPs. Once having been formed, those clusters are unbreakable by purely thermal motion. While trimers and multi-particle clusters are assumed to take configurations with low magnetic momnets (nearly closed flux state), the dimers do not. They rather behave as elongated particles with the magnetic moment along their major axis. In the isotropic phase, the magnetic moments of single MNPs and of those united in dimers are disordered due to the orientational Brownian motion; Fig. 6a displays a schematic representation of this state; for simplicity, the clusters with more than three particles are not shown. The magnetic moments of single MNPs and dimers are modulated by the probing ac magnetic field yielding \(\chi'_I\), while clusters with near-zero magnetic moment virtually do not contribute. Such a scenario could eventually explain why there is a substantial difference between the estimated \(\gamma_0\) in eqn (9) and the measured static and dynamic susceptibilities [see eqn (10) and (1)].

Our interpretation is that the application of a strong dc magnetic field in the isotropic phase aligns the magnetic moments in the direction of \(H_{dc}\), as shown in Fig. 6b. For triangular trimers, however, the parallel magnetic moments correspond to an energetically unfavored configuration; these are unstable and prefer to disintegrate into a dimer and a single MNP which repel each other. Similarly, larger aggregates may also become aligned by strong fields and may lose particles due to repulsion forces. When \(H_{dc}\) is switched off, the magnetic moments become disoriented by Brownian rotation, while multi-particle clusters go back to their closed-flux shapes. Due to the partial disintegration of the trimers and other multi-particle clusters, the magnetic field-treated isotropic sample (Fig. 6c) contains more particles contributing to \(\chi'\) (single MNPs and dimers) and fewer non-contributing
ones (trimers and higher-order clusters) than the untreated FN (Fig. 6a). As a result, a higher ac susceptibility, $\chi_{ac}$ of eqn (2), should be detected.

When this system is cooled down and driven through the I–N transition, all the suspended solid entities—single particles as well as clusters of all kinds—induce disclinations in the nematic structure around themselves.5,8 Due to that, on the one hand, additional binding forces between particles may appear6,7 and, on the other hand, the matrix accumulates extra orientation-elastic energy and strives to get rid of this excess by expelling the particles. In chemical terms, this means a diminution of the particle solubility, which manifests itself as enhanced particle susceptibility to the value measured prior to the application of the dc bias field. After that, the sample could be “biased” again by repeated applications of the dc field in the isotropic phase.

The proposed phenomenological explanation associates the discovered effect with the aggregation of nanoparticles in the course of the isotropic-to-nematic phase transition and their disaggregation under the influence of a dc (bias) magnetic field. Therefore, it is not surprising that the effect is inherent only to ferronematics and it has no analogues in undoped liquid crystals.

Although here we presented the experimental results for a single concentration of magnetite nanoparticles in a specific liquid-crystalline matrix, the reported effect of biasing appears to be generic: our preliminary experiments on composites based on various liquid-crystalline matrices and various ferrite fillers, reveal the same effect.

Finally, it has to be noted that the above presented phenomenological description, though plausible, still needs further experimental, and/or numerical verification. The experimental verification of the homogeneity of the FN, as well as of the presence (or absence) of the sub-micrometer sized particle clusters is extremely challenging due to the very low volume fraction of the MNPs. We could not get a signal from the MNPs either by atomic force microscopy (AFM) nor by small angle neutron scattering (SANS). Similarly, no decisive evidence is expected from small angle X-ray scattering (SAXS) measurements, especially considering that the concentration of MNPs in our FN is below the lowest concentration limit for such measurements.36 The cryo-TEM technique37 could eventually provide experimental evidence in favor (or against) the phenomenological description presented here. Numerical verification is also demanding, due to the complexity of our colloidal system compared to isotropic magnetic fluids. In FNs, besides the concentration and the polydispersity of MNPs, one has to consider and to take into account the elasticity of the nematic matrix, the creation (and annihilation) of TDs, the interactions between the TDs and the MNPs, etc.

4 Conclusions

We have demonstrated that a small dc magnetic field (of the order of several Oe) applied in the isotropic phase modifies the magnetic susceptibility of a ferronematic by about 10%. This enhanced value subsists for a long time (~hours) while the sample is kept in the isotropic phase. Driving it through the isotropic-to-nematic phase transition resets the magnetic susceptibility to the value measured prior to the application of the dc bias field. After that, the sample could be “biased” again by repeated applications of the dc field in the isotropic phase.

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Although here we presented the experimental results for a single concentration of magnetite nanoparticles in a specific liquid-crystalline matrix, the reported effect of biasing appears to be generic: our preliminary experiments on composites based on various liquid-crystalline matrices and various ferrite fillers, reveal the same effect.

Finally, it has to be noted that ac susceptibility measurements have also been performed on a water-based magnetic fluid (MF). Upon the application of a dc magnetic field bias above the freezing point of the MF a sudden decrease of $\chi'$ has been observed on cooling at the phase transition. On heating, however, at the melting point a sudden increase in $\chi'$ has also been detected (i.e. the process turned out to be completely
reversible in case of the MF). This observation is in contrast to the non-reversible effect in FNs, indicating that the biasing mechanisms differ in MFs and in FNs, and supporting the statement that the peculiarities of the nematic phase are crucial in understanding the phenomenon.

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