The structural instabilities in ferronematic based on liquid crystal with negative diamagnetic susceptibility anisotropy

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ABSTRACT

The studied ferronematic is a nematic liquid crystal (ZLI1695) of low negative anisotropy of the diamagnetic susceptibility ($\chi_a < 0$) doped with the magnetic particles Fe_3O_4. Structural instabilities are interpreted within Burylov and Raikher's theory. The high magnetic fields were oriented perpendicular (Freedericksz transition) or parallel to the initial director. Using capacitance measurements the Freedericksz threshold magnetic field of the ferronematic B_{FN}, and the critical magnetic field B_{max}, at which the initial parallel orientation between the director and the magnetic moment of magnetic particles breaks down, have been determined. The values of these quantities have been used to estimate the surface density of the anchoring energy W of liquid crystal molecules on the surface of the magnetic particles. The obtained values indicate a soft anchoring of the liquid crystal on the magnetic particles with a preferred parallel orientation of the magnetic moment of magnetic particles and the director.

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1. Introduction

An idea of enhancing the magnetic susceptibility of liquid crystals by doping them with fine magnetic particles was firstly given by Brochard and de Gennes in 1970 when the authors formulated the theory of ferronematics, i.e. the magnetic suspensions in nematic liquid crystals [1]. In the first experimental paper, Rault et al. [2] reported the basic magnetic properties of a suspension of rod-like magnetic particles γ-Fe_2O_3 in the liquid crystal 4′−methoxybenzylidene − 4 − n − butylaniline (MBBA). Later, based on the predictions given in [1], first lyotropic [3–5] and then thermotropic [6,7] ferronematics have been prepared and studied. An important question solved in the theory of magnetic suspensions in liquid crystals was that of the equilibrium orientation of the magnetization of a rod-like magnetic particle with respect to the host liquid crystalline matrix. The Brochard–de Gennes theory provided a universal conclusion: the equilibrium orientation of the particle (and its magnetic moment m) is parallel to the liquid crystal director n (co-alignment postulate $m \| n$) [1]. However, the experiments in which the response of the thermotropic ferronematics to the applied magnetic field was investigated have showed, that the co-alignment postulate mostly does not fulfil. In an attempt to explain this fact Burylov and Raikher [8] have re-analysed the Brochard–de Gennes theory concluding that its applicability is limited to the rigid-anchoring condition

$$\omega \equiv \frac{Wd}{K} \gg 1. \tag{1}$$

Here W is the surface density of the anchoring energy at the magnetic particle–nematic boundary, d is the typical particle size, and K is Frank's orientation-elastic modulus of a given liquid crystal. In general, depending on the geometry of the problem one or more of the splay, bend and twist modulus should be considered. According to Burylov and Raiker [8], for systems with $\omega \leq 1$ (soft-anchoring) the equilibrium orientation of magnetic particle could be either parallel or perpendicular to the director ($m \perp n$). Next, Burylov and Raikher have considered the instability of the uniform texture in thermotropic ferronematics exposed to an external magnetic or electric field applied perpendicular to the initial orientation of the nematic director, known as Freedericksz transition, and derived the expressions for its critical field in different geometries [9,10].

In our previous works we have studied the influence of the magnetic field on the electric Freedericksz transition and the structural instabilities in different ferronematics exposed to

the magnetic field. Our experiments have shown that in the case of nematic liquid crystals doped with magnetic particles, the value of the critical magnetic field of the magnetic Fredericksz transition can either increase (as was observed for the matrix of 4−n−octyl−4′−cyanobiphenyl (8CB)) [11,12] or decrease (as for 4−(trans−4′−n−hexylcyclohexyl)−isothiocyanatobenzene (6CHBT) and MBBA matrixes) [13,15,16], in comparison to the values corresponding to that of the pure nematic liquid crystal. We have found that this different behaviour depends on the initial orientation between the director **n** of the liquid crystal and the magnetic moment **m** of the magnetic particles. In the case of a co-linear orientation a decrease was observed while in the case of the perpendicular condition an opposite behaviour was observed. In all these experiments the anisotropy of the diamagnetic susceptibility of the nematic liquid crystal was positive ($\chi_a > 0$). All achieved experimental results were in qualitative agreement with Burylov–Raikher's estimations.

The aim of the present work is to extend the study of structural instabilities and their interpretation within Burylov–Raikher's theory, onto a ferronematic based on a liquid crystal with very low and negative anisotropy of the diamagnetic susceptibility ($\chi_a < 0$), exposed to the magnetic fields oriented perpendicular or parallel to the initial director.

2. Experiment

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. 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 °C and 25% NH_4OH was added. The precipitate was isolated from the solution by magnetic decantation by washing with water. The magnetic properties were obtained by magnetization measurements using a vibrating sample magnetometer (VSM) and the size and morphology of the particles were determined by transmission electron microscopy (TEM) and atomic force microscopy (AFM) working in taping mode. The mean diameter of the obtained magnetic nanoparticles was 11.6 nm. TEM imagine and histogram of size distribution are in Figs. 1 and 2, respectively.

The used liquid crystal, a 4−alkyl−4′−cyanobicyclohexyl mixture (ZLI1695) was obtained from Merck Co. The temperature
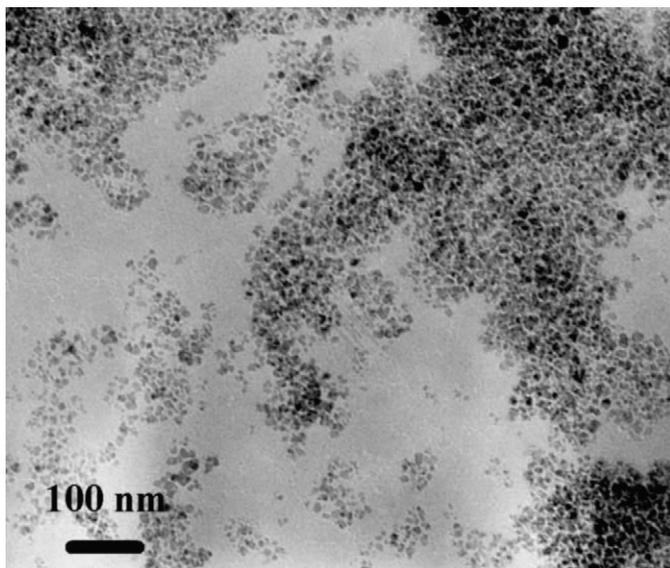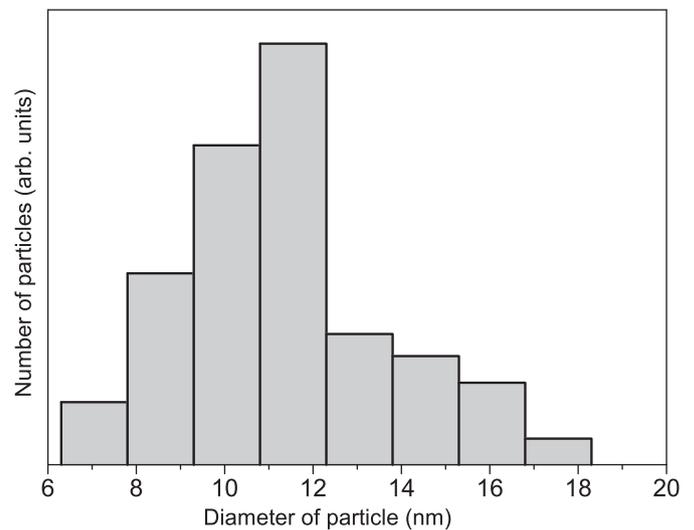

Fig. 1. TEM image of magnetic nanoparticles.

Fig. 2. Histogram of size distribution of magnetic nanoparticles.

of the nematic—isotropic transition was found to be $T_{N-I} = 73.5$ °C, the splay elastic constant $K_{11} = 7$ pN, and the anisotropy of diamagnetic susceptibility $\chi_a = \chi_\parallel - \chi_\perp = -2.55 \times 10^{-8}$. The magnetic Fe_3O_4 particles used in the ferronematics were coated with a surfactant (oleic acid and dodecyl benzene sulphonic acid) for suppressing their aggregation. The doping of the nematic sample with magnetic suspension was simply done by adding this suspension to the liquid crystal under continuous stirring. The measurements were performed with ferronematics with volume concentrations of magnetic particles $\phi_1 = 2 \times 10^{-4}$, $\phi_2 = 5 \times 10^{-4}$ and $\phi_3 = 1 \times 10^{-3}$. The structural transitions in ferronematic samples were monitored by capacitance measurements in a capacitor made of indium-tin-oxide (ITO) coated glass electrodes (LINCAM Co.). The capacitor with the electrode area approximately 1 cm × 1 cm was connected to a regulated thermostat system, the temperature was stabilized with the accuracy of 0.05 °C. The distance between the electrodes (sample thickness) was $D = 18 \mu m$. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling. The stability of the samples in the strong magnetic fields was verified by repeating the capacitance measurements after 5 months on the same samples, with reproducible results. On account of the very low magnetic susceptibility of the used liquid crystal, high magnetic fields (>3 T) were used to induce a structural instability of its texture. In the experiment the liquid crystal had a planar initial alignment; i.e. the director was parallel to the capacitor electrodes (see Fig. 3). It should be pointed out for the next consideration that the minimal value of capacitance is observed for planar alignment while the maximal value for homeotropic alignment, i.e. when the director **n** is perpendicular to the capacitor electrodes. Freedericksz transitions in magnetic fields were studied in the assumed experimental geometry shown in Fig. 3 at the temperature 35 °C.

3. Results and discussion

As shown in Fig. 3, in our experiments we are dealing with two orientational effects caused by the magnetic field applied to the system studied. It is due to the fact that the system is composed of two different magnetic entities: the diamagnetic mesogenic molecules (host) and magnetic particles (guest). The two entities show a quite different orientational behaviour on the magnetic field applied: the diamagnetic molecules of the nematic liquid
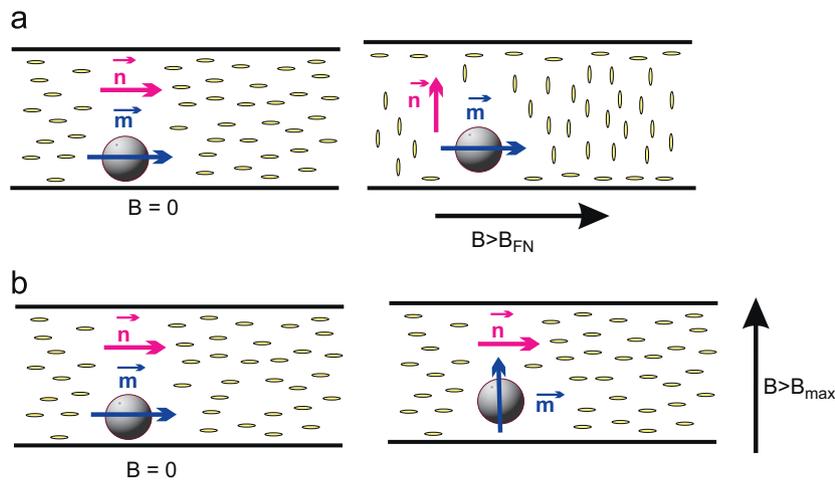
Fig. 3. Cross section of the cell in the initial state, after application of the magnetic field $B > B_{FN}$ parallel to the surface of the electrodes and after application of the magnetic field $B > B_{max}$ perpendicular to the surface of the electrodes.

crystal will orient themselves perpendicular to the field direction due to the negative anisotropy of the diamagnetic susceptibility while the magnetic moment of the guest particles align along the magnetic field direction. That relatively simple orientational picture is, however, disturbed by the mutual interactions between the diamagnetic molecules and magnetic particles (molecular anchoring on the particles surface) and between the molecules and the surface of the measuring cell (molecular anchoring on the cell electrodes surfaces). As a consequence of these interactions only magnetic fields exceeding a certain critical value may induce reorientation. This critical magnetic field depends on the initial (at $B=0$) mutual orientation of the entities present in the system studied as well as on the anchoring energies. So, the studies of that problem can lead to the determination of the anchoring energies, the quantities very important in practical uses of nematic liquid crystals and ferronematics. As presented in Fig. 1, the initial geometry of our experiment is very simple: the director n and the magnetic moment m are parallel to each other; the arrangement is forced by a special treatment of the cell electrodes causing a planar orientation of the liquid crystal molecules. Next, the magnetic field is applied parallel to the director n (Fig. 3a right) or perpendicular to it (Fig. 3b right). In the first case, due to the negative anisotropy of the diamagnetic susceptibility of the mesogenic compound studied, applying the magnetic field to the system is followed by the director reorientation from the planar configuration to the homeotropic one. However, as we mentioned above, the reorientation can take place only above a threshold magnetic field B_{FN}. In this geometry, as presented in Fig. 3, a classical Freedericksz transition is observed and the critical magnetic field B_{FN} depends on the concentration of the magnetic particles in the nematic liquid crystal.

According to our experiments the critical magnetic field B_{FN} of the thermotropic ferronematics is higher than the Freedericksz threshold magnetic field B_{LC} of the pure liquid crystal host. This increase has been described by Burylov and Raikher [9]. For the initial geometry showed in Fig. 3

$$B_{FN}^2 - B_{LC}^2 = \frac{2\mu_0 W \phi}{|\chi_a| d}, \tag{2}$$

with

$$B_{LC}^2 = \left(\frac{\pi}{D}\right)^2 \frac{\mu_0 K_{11}}{|\chi_a|}, \tag{3}$$

where ϕ is the volume concentration of the magnetic particles, χ_a is the anisotropy of the diamagnetic susceptibility, D is the
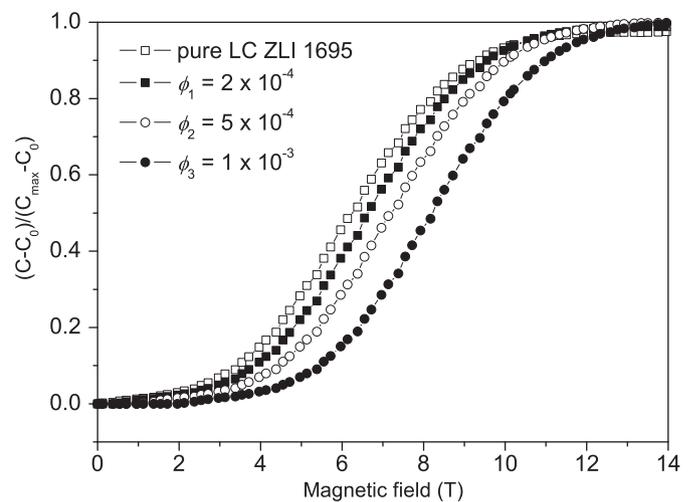
Fig. 4. Reduced capacitance dependence of pure liquid crystal and liquid crystal doped with different volume concentrations of spherical particles on magnetic field applied parallel to the surface of electrodes.

thickness of the ferronematic layer and K_{11} is the splay elastic constant of the nematic corresponding to the used geometry. In order to allow an easier comparison of the behaviour of various samples it is convenient to introduce a reduced capacitance C_r by the formula

$$C_r = \frac{(C - C_0)}{(C_{max} - C_0)}, \tag{4}$$

where C is the capacitance measured at a given magnetic field B, C_{max} is capacitance at the maximal value of B, and C_0 corresponds to $B=0$. Fig. 4 shows the magnetic field dependence of the reduced capacitance measured for the pure liquid crystal as well as for the liquid crystal doped with different volume concentrations of the magnetic nanoparticles ($\phi_1 = 2 \times 10^{-4}$, $\phi_2 = 5 \times 10^{-4}$ and $\phi_3 = 1 \times 10^{-3}$).

We start from a planar aligned cell. If we suppose a parallel initial orientation of the director and the magnetic moment of magnetic particles, the liquid crystal molecules anchored at the surfaces of the magnetic particles keep their magnetic moments oriented parallel to the electrodes (Fig. 3a and b left). In capacitance measurements this manifests itself in minimum of capacitance.

In the first experiment, the external magnetic field was parallel to the initial director alignment, along the equilibrium ferronematic texture. This magnetic field does not alter the direction of the magnetic moments. However, as the magnetic field increases, the director tends to realign in the direction perpendicular to the magnetic field due to the negative diamagnetic susceptibility of the nematic host (Fig. 3a right). This Freedericksz transition starts in the ferronematics at the critical field intensity B_{FN}. At fields exceeding B_{FN} the initially parallel orientation between the magnetic moments of the magnetic particles and the bulk director brakes down. In capacitance measurements the director realignment results in an increase of the capacitance. It is clearly seen in Fig. 4 that the magnetic field induced deformation occurs at higher field in the ferronematics than in the pure host; i.e. $B_{FN} > B_{LC} = 3.41$ T. Moreover, B_{FN} becomes larger with increasing volume concentration of the magnetic particles (as presented in Table 1) indicating that the magnetic particles exert a stabilizing torque on the director which acts against the destabilizing diamagnetic interactions. The origin for this hindrance of the director rotation lies in the bounding between the magnetic moment of magnetic particles and the liquid crystal molecules anchored on the surface of particles. This result confirms our assumption on the parallel initial orientation $\mathbf{m} \| \mathbf{n}$.
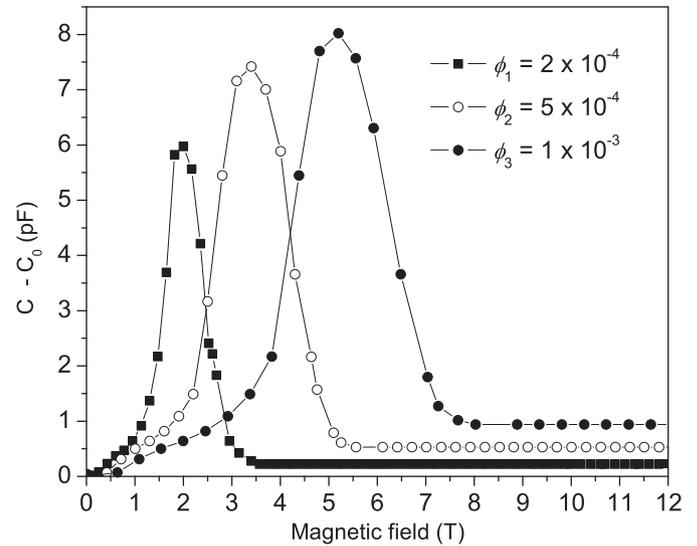
In the next experiment, the magnetic field was applied perpendicular to the electrodes, i.e. perpendicular to the initial alignment of the director and the magnetic moments of the magnetic particles. In this case upon applying the magnetic field the magnetic moments of magnetic particles will rotate toward the direction of the field (Fig. 3b right). As the magnetic moments and director prefer a parallel initial orientation, the liquid crystal molecules anchored at the surfaces of the magnetic particles should follow rotation of $\mathbf{m}$ thus inducing a distortion of the director field around the magnetic particles.

The distortion manifests itself in the increase of the capacitance as is shown in Fig. 5. It is also seen, however, that capacitance grows with $\mathbf{B}$ only up to some critical field intensity B_{max}, where it reaches a maximal value. On further increase of the magnetic field, i.e. $B > B_{max}$, the capacitance decreases again. This latter indicates that the diamagnetic torque arising due to the negative χ_a of the host liquid crystal overcomes the effect of the initial parallel bonding between the magnetic moments of the magnetic particles and the director. Consequently at high magnetic fields the initial planar director alignment is restored in the cell resulting in $\mathbf{m} \perp \mathbf{n}$. It is clearly seen from Fig. 5 as well as from Table 1 which lists the measured values of B_{FN} and B_{max} for ferronematics with different volume concentrations of the magnetic particles that a higher doping concentration increases B_{max} substantially. These results imply that the admixture of magnetic particles to this kind of liquid crystal ($\chi_a < 0$) hinders the reorientation of the director by the external magnetic field.

The magnetic field corresponding to the maximum in capacitance could be calculated theoretically using the free energy expression [9]. The magnetic field corresponding to the maximum in capacitance could be qualitatively estimated from comparison of magnetic energy from the density of magnetic

Fig. 5. Dependence of the change of the capacitance of liquid crystal doped with different volume concentrations of spherical particles on magnetic field applied perpendicular to the surface of electrodes.

Table 2
The surface density of the anchoring energy W calculated from B_{FN} and B_{max} for different volume concentrations of magnetic particles.

Magnetic particles volume concentration	$W_{B_{FN}}$ (N/m)	$W_{B_{max}}$ (N/m)
$\phi_1 = 2 \times 10^{-4}$	2.00×10^{-6}	2.02×10^{-6}
$\phi_2 = 5 \times 10^{-4}$	2.13×10^{-6}	2.33×10^{-6}
$\phi_3 = 1 \times 10^{-3}$	2.20×10^{-6}	2.73×10^{-6}

energy of liquid crystal which is

$$\frac{B_{max}^2}{2\mu_0}, \tag{5}$$

with density of anchoring energy, which is roughly

$$\frac{W}{d}\phi. \tag{6}$$

From this comparison we obtain

$$B_{max}^2 \approx \frac{2\mu_0 W\phi}{|\chi_a|d}. \tag{7}$$

Comparing this result with Eq. (2) the following identity can be picked up:

$$B_{max}^2 \approx B_{FN}^2 - B_{LC}^2. \tag{8}$$

The experimental test of this identity have shown, as one can see from Table 1, that Eq. (8) fulfils nicely for the lowest concentration of the magnetic particles, but holds less for the higher concentrations.

The experimentally obtained B_{FN} and B_{max} values have also been used to estimate the surface density of the anchoring energy W of the liquid crystal molecules on the magnetic particle surface. Table 2 summarizes the W values obtained using Eqs. (2) and (7). It is seen that the values obtained for different volume concentrations of magnetic particles are in fairly good agreement.

The knowledge of W allows for calculating the parameter ω too. The obtained values of parameter ω are of the order 10^{-3}, i.e. $\omega < 1$ that characterizes soft anchoring of nematic molecules on the surfaces of magnetic particles. This type of anchoring permits both parallel and perpendicular orientation of the magnetic moment of magnetic particles with respect to the director.

Table 1
The critical fields B_{FN} and B_{max} for different volume concentrations of magnetic particles.

Magnetic particles volume concentration	B_{FN} (T)	B_{max} (T)	$(B_{FN}^2 - B_{LC}^2)/B_{max}^2$
$\phi_1 = 2 \times 10^{-4}$	3.9	2.0	0.97
$\phi_2 = 5 \times 10^{-4}$	4.6	3.4	0.77
$\phi_3 = 1 \times 10^{-3}$	5.6	5.2	0.61

Table 3
The calculated surface density of the anchoring energy W, parameter ω, and the initial orientation between the magnetic moment of magnetic particles and the director for different ferronematics.

Liquid crystal	W (N/m)	ω	Initial orientation between $\boldsymbol{m}$ and $\boldsymbol{n}$	Ref.
8CB	$\sim 10^{-4}$	$\sim 10^{0}$	Perpendicular	[14]
MBBA	$\sim 10^{-7}$	$\sim 10^{-3}$	Parallel	[15]
6CHBT	$\sim 10^{-5}$	$\sim 10^{-1}$	Parallel	[16]
HAB	$\sim 10^{-3}$	$\sim 10^{-1}$	Parallel	[17]
ZLI1695	$\sim 10^{-6}$	$\sim 10^{-3}$	Parallel	

For a comparison with other ferronematics, in Table 3 we summarized the W and ω values, as well as initial orientation between the magnetic moment of magnetic particles and the director obtained from our previous experiments [14–17] for different nematics doped with nearly spherical magnetic nanoparticles of the same size. It is seen that the characteristics of ZLI 1695 do not differ significantly from that of other ferronematics.

The surface anchoring energy density W depends not only on the liquid crystal but on the type of the surface too. Data are mostly available for the sandwich cell geometry where the nematic layer is enclosed between two glass surfaces coated with orienting layers. Typically for strongly anchored planar orientation one obtains $W \approx 10^{-5}-10^{-4}$ N/m [18,19], while for the considerably weaker homeotropic alignment $W \approx 10^{-7}-10^{-6}$ N/m has been measured [20]. We note, however, that in addition W has a temperature dependence which is especially strong close to T_{N-I} [21].

4. Conclusion

The influence of admixing magnetic particles on the structural instabilities was studied in planar aligned ZLI1695-based ferronematics with magnetic field either parallel or perpendicular to the initial director. It was shown that in both geometries doping with magnetic particles hinders the reorientation of the director by magnetic field. The relevant critical magnetic fields (B_{FN} or B_{max}) of prepared ferronematics become larger with increasing volume concentration of the magnetic particles. These results confirm the preference for the initial parallel orientation between magnetic moment of magnetic particles and the director. The obtained results are in good agreement with Burylov–Raikher's theory. The anchoring energies calculated from the experimental results indicate soft anchoring.

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