Magneto-orientational effects in nematic liquid crystals doped with goethite nanoparticles

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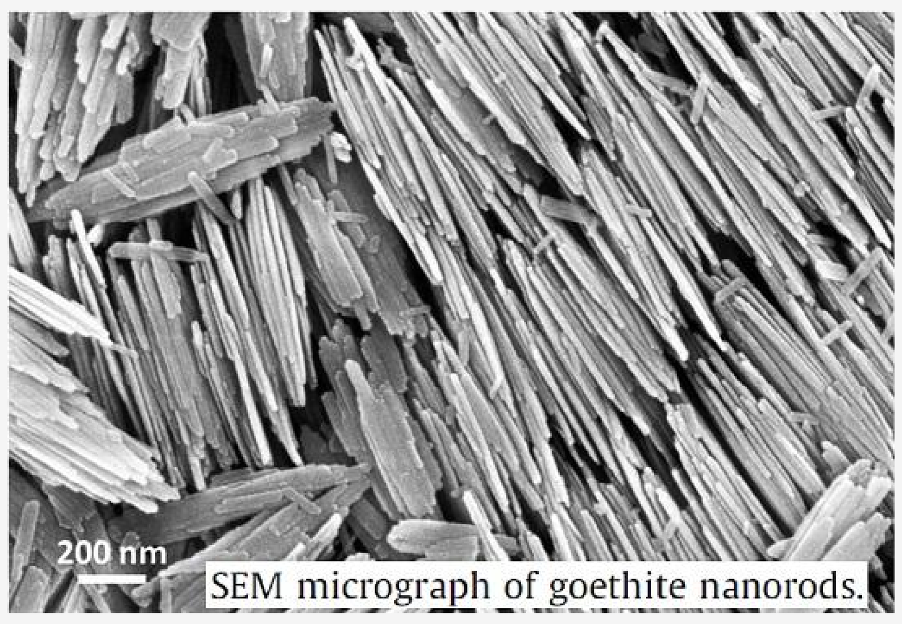
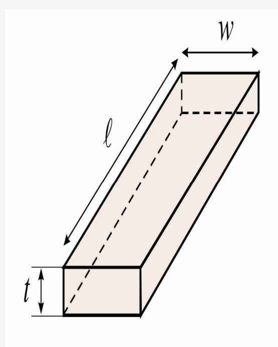
SUMMARY

We present complete theoretical and experimental studies of orientational magnetically induced Fréedericksz transitions in suspensions of goethite lathlike nanorods in a nematic liquid crystal (NLC) 4-(trans-4-n-hexylcyclohexyl)-isothiocyanato-benzene (6CHBT), known as ferronematics (FN`s) [1, 2]. The magnetically induced behavior of this system strongly depends (*i*) on orientational coupling between nematic matrix and nanoparticles, (*ii*) on specific magnetic properties of goethite impurity, and (*iii*) on initial magnetic properties of the sample as a whole. It has been shown that the orientational coupling between nematic matrix and nanoparticles is determined by the anchoring forces between the nematic molecules and the magnetic nanoparticles, which are easily oriented by the external magnetic field. The direction of this orientation depends on the magnetic properties of goethite nanorods having two components of magnetic moments – the remanent magnetic moment along the main axes of the particles and the induced magnetic moment perpendicular to the main axes. Therefore, the nanoparticles tend to orient parallel and perpendicular to the external field in the low or high magnetic field region, respectively. The magnetic orientation effects are further influenced by the initial magnetic properties of the samples. Two types of samples with different magnetic properties were prepared. A so-called compensated sample with zero initial magnetization was obtained after cooling the system from isotropic to nematic phase in the absence of a magnetic field. A magnetized sample was prepared during magnetic field application. The field induced structural responses in the so called splay geometry of the cells were investigated by electrical capacitance measurements. The magnetically induced transitions demonstrated two different types of orientational behavior of the samples. The Fréedericksz transition in the compensated ferronematic occurred in higher magnetic field in comparison with pure nematic while the magnetized ferronematic sample shown well measurable response in capacitance to the applied magnetic field, even much below the Fréedericksz threshold in usual 6CHBT. Full theoretical descriptions of such behaviours of compensated and magnetized ferronematic samples are presented and all observed dependencies of the cells capacitance on magnetic field are numerically calculated. A comparative analysis shows very well qualitative and quantitative agreement between theoretical results and experimental data. Due to this the material parameters of the investigated ferronematic system with goethite nanoparticles are estimated.

Properties of goethite (α-Fe00H) nanoparticles



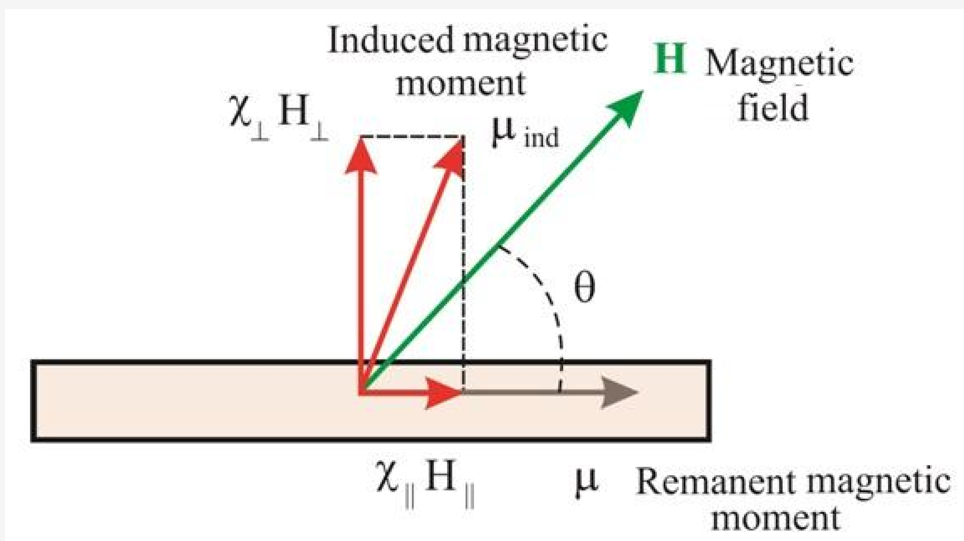
SEM micrograph of goethite nanorods.



Mean sizes:
$l \times w \times t$ = 350 × 25 × 10 nm.
Remanent magnetic moment: $\mu \sim 1000 \cdot \mu_B$, where μ_B is the Bohr magneton.
Diamagnetic anisotropy:
$\chi_p = \chi_{\|} - \chi_{\perp} \approx -5 \cdot 10^{-4}$.
Concentration in FNs: $\phi = 10^{-2}$ vol%

The magnetic energy of an individual particle

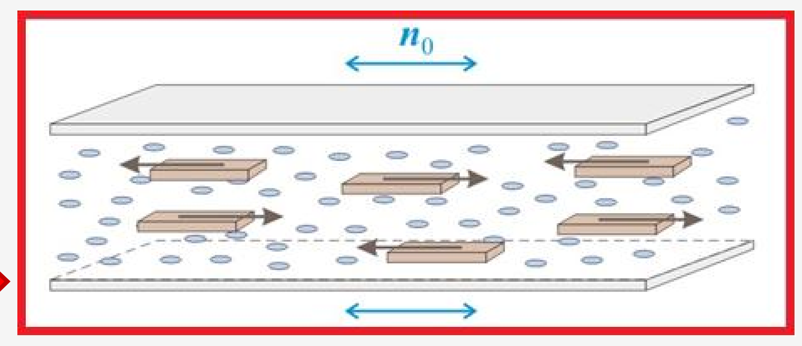
$$E_m(\theta) = -\mu B \cos\theta - \frac{\chi_p v}{2\mu_0} B^2 \cos^2\theta$$



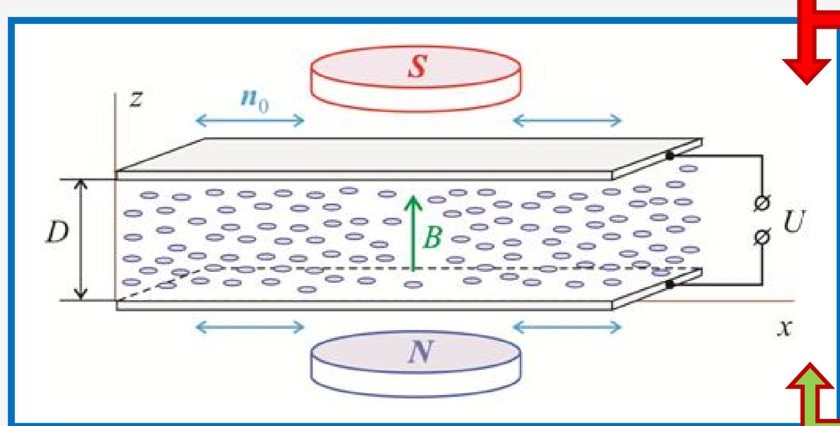
The particles align parallel to a weak field (<350 mT), but realign perpendicular to a relatively strong field (>350 mT).

Geometry of FN cells and their initial magnetization

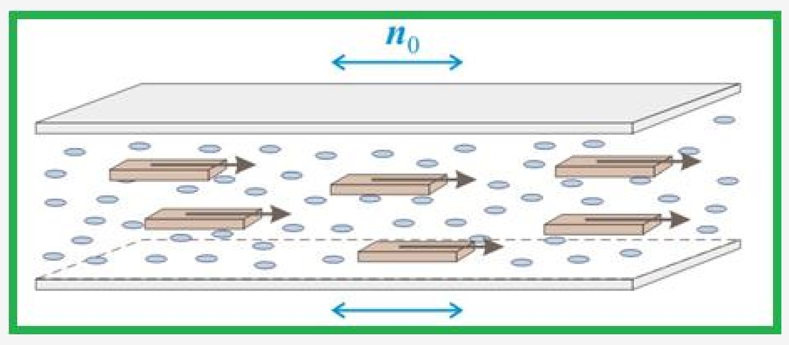
Cooling the FN in zero magnetic fields, it creates an approximately equal fraction of particles with their remanent magnetic moments oriented parallel and antiparallel to local director **n**.



The compensated ferronematic with zero initial magnetization



The magnetized state is characterized by co-alignment of remanent magnetic moments of particles in each point of the sample. It was reached when a magnetic field is applied during cooling of the system from isotropic to nematic phase.



The magnetized ferronematic with non zero initial magnetization

Theoretical models

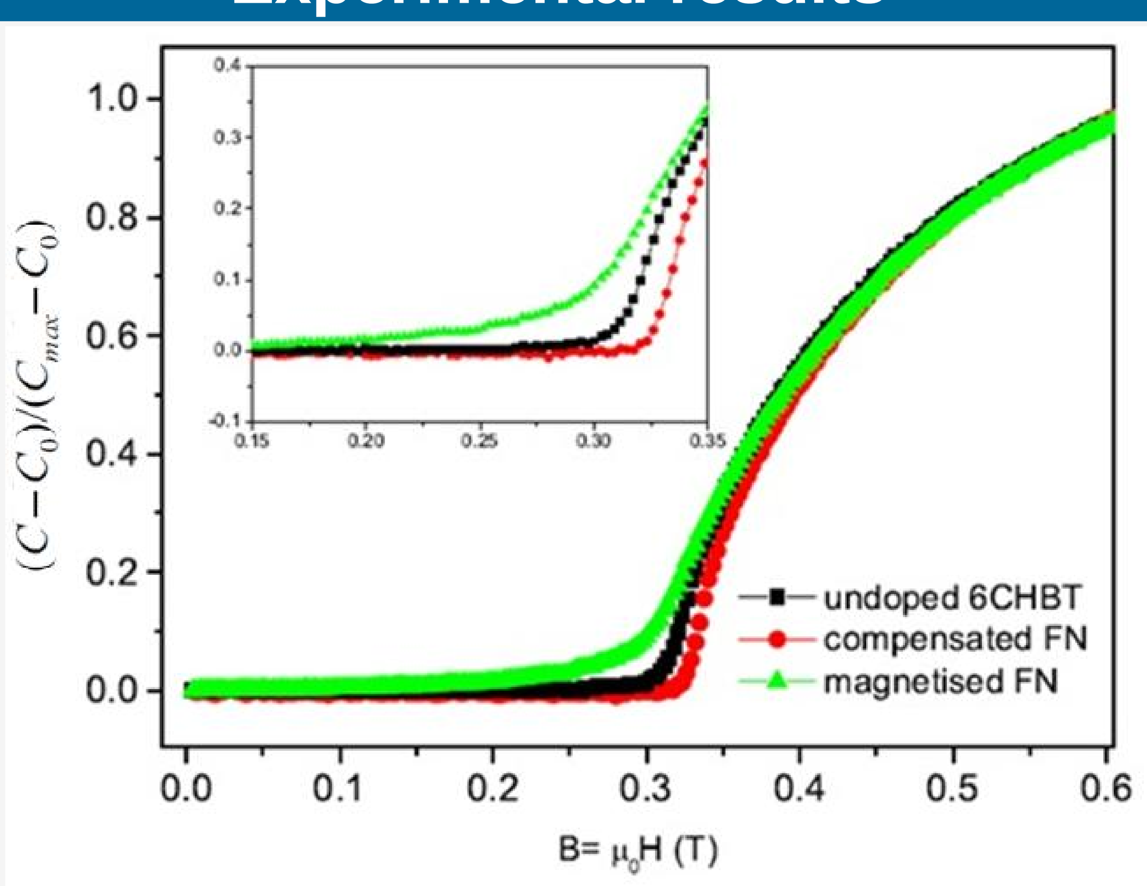
The full free energy functional of the magnetized FN

$$F_{mag} = \int dV \left\{ \underbrace{\frac{1}{2}\left[K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2\right]}_{\text{elastic energy of NLC}} \underbrace{- \frac{\chi_a}{2\mu_0}(\boldsymbol{n}\cdot\boldsymbol{B})^2}_{\text{diamagnetic energy of NLC}} \underbrace{- \frac{\mu\phi}{v}\cdot(\boldsymbol{m}\cdot\boldsymbol{B}) - \frac{\chi_p\phi}{2\mu_0}\cdot(\boldsymbol{m}\cdot\boldsymbol{B})^2}_{\text{magnetic energy of particles}} \underbrace{- \frac{WS\phi}{v}\cdot(\boldsymbol{m}\cdot\boldsymbol{n})^2}_{\text{coupling energy}} + \underbrace{\frac{k_B T}{v}\phi\ln\phi}_{\text{entropy term}} \right\}$$

The full free energy functional of the compensated FN

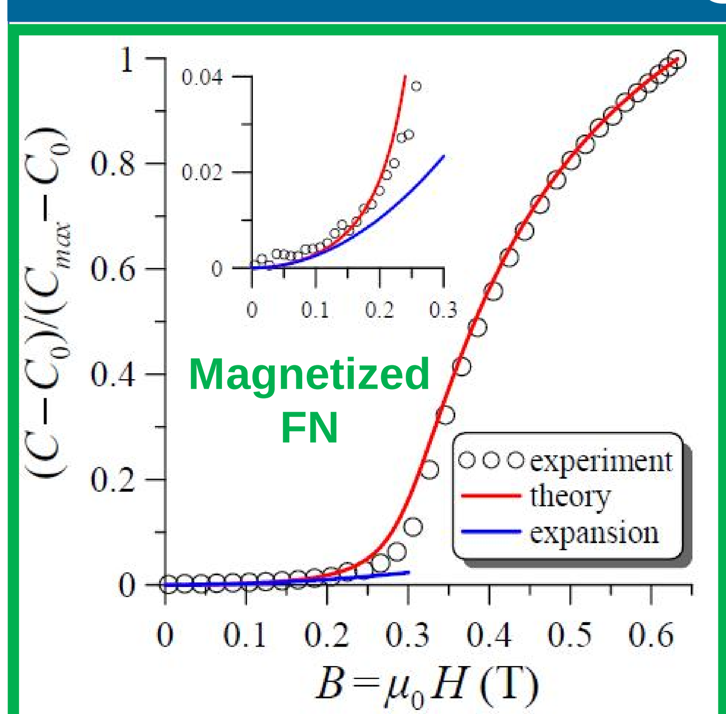
$$F_{comp} = \int dV \left\{ \underbrace{\frac{1}{2}\left[K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2\right]}_{\text{elastic energy of NLC}} \underbrace{- \frac{\chi_a}{2\mu_0}(\boldsymbol{n}\cdot\boldsymbol{B})^2}_{\text{diamagnetic energy of NLC}} \right.$$
$$\left. \underbrace{- \frac{\mu}{v}(\phi_+ - \phi_-)\cdot(\boldsymbol{m}\cdot\boldsymbol{B}) - \frac{\chi_p}{2\mu_0}(\phi_+ + \phi_-)\cdot(\boldsymbol{m}\cdot\boldsymbol{B})^2}_{\text{magnetic energy of particles}} \underbrace{- \frac{WS}{v}(\phi_+ + \phi_-)\cdot(\boldsymbol{m}\cdot\boldsymbol{n})^2}_{\text{coupling energy}} + \underbrace{\frac{k_B T}{v}(\phi_+ \ln\phi_+ + \phi_- \ln\phi_-)}_{\text{entropy term}} \right\}$$

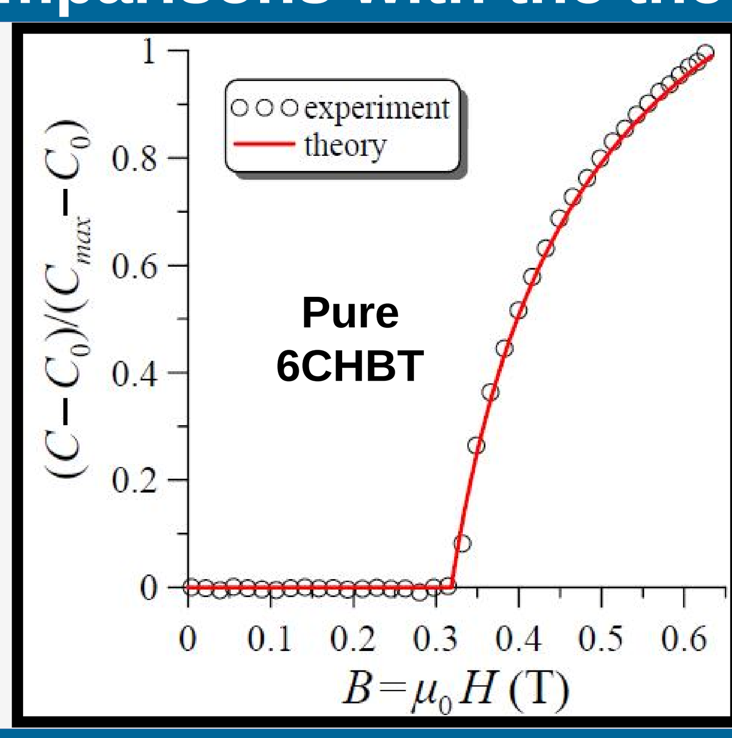
Experimental results

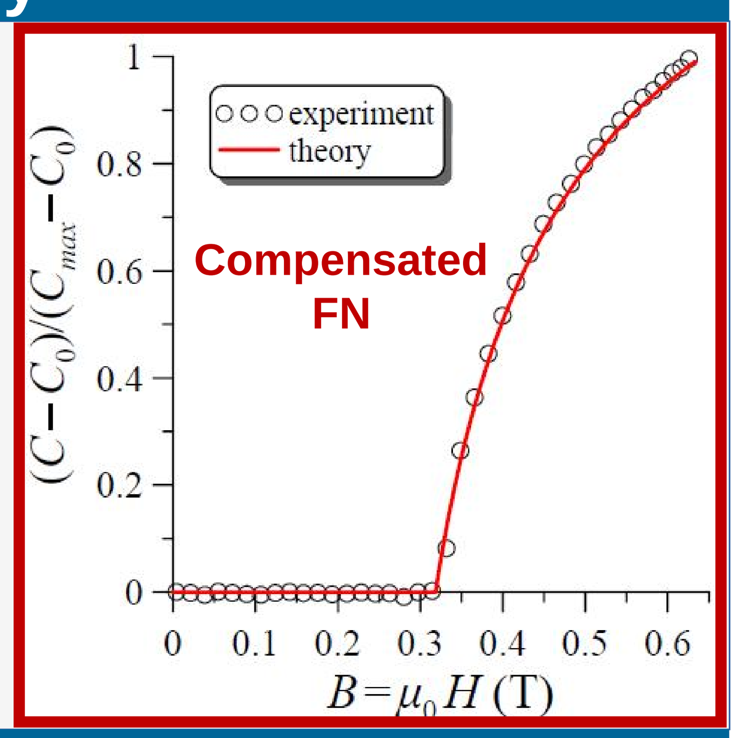


The Fréedericksz transition in the compensated ferronematic occurred in higher magnetic field in comparison with pure nematic while the magnetized ferronematic sample shown well measurable response in capacitance to the applied magnetic field, even much below the Fréedericksz threshold in usual 6CHBT.

Comparisons with the theory







The estimated material parameters of the ferronematic

parameters of nematic matrix 6CHBT				parameters of goethite nanorods				anchoring (coupling) energy density
elastic constants		dielectric anisotropy	diamagnetic anisotropy	mean sizes	volume fraction	remanent magnetic moment	diamagnetic anisotropy	
K_{11}(N)	K_{33}/K_{11}	ε_a	χ_a	$l \times w \times t$(nm)	ϕ	μ(J/T)	χ_p	W(J/m^2)
$6.405 \cdot 10^{-12}$	1.1	6.73	$3.31 \cdot 10^{-7}$	350 × 25 × 10	10^{-4}	$10^3 \mu_B$	$-5 \cdot 10^{-4}$	4.5×10^{-7}

References

1. *Kopčanský P., Gdovinová V., Burylov S., Burylova N., Voroshilov A., Majorošová J., Agresti F., Zin V., Barison S., Jadżyn J., Tomašovičová N.* The influence of goethite nanorods on structural transitions in liquid crystal 6CHBT // J. Magn. and Magn. Mater.– 2018. – **459**, P 26-32.
2. *Burylov S., Petrov D., Lacková V., Zakutanská K., Burylova N., Voroshilov A., Skosar V., Agresti F., Kopčanský P., Tomašovičová N.* Ferromagnetic and antiferromagnetic liquid crystal suspensions: Experiment and theory// J. Mol. Liq.–2021.–**321**, 114467.