FREEDERICKSZ TRANSITION IN NEMATIC LIQUID CRYSTALS WITH CARBON NANOMATERIALS

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Carbon nanoparticles are some of the most studied nanoparticles by chemists, physicist and engineers all around the world. Their unique physical properties including mechanical strength, electrical or thermal conductivity indicate a great potential for material science applications. While graphene sheets present a good dispersion in nematic liquid crystal and seem to decrease the Freedericksz transition reducing the power consumption of LCDs, the nanotubes increase the stability of the host being more suitable for phase modulators. In both cases, we need only small amounts of substance, so the beam intensity is not affected, and the device quality is still very good.

Keywords: nanomaterials, carbon nanotubes, graphene, liquid crystals

1. Introduction

Since the nanoparticle's discovery, it was proved that their properties are significant different from those of bulk material from the same substance. They were used in different devices, including in liquid crystals to improve the stability or the electro-optical properties of LCDs or LC-phase modulators, diffraction gratings, etc. [1-8] Carbon based nanomaterials, such as graphene, fullerenes, nanotubes benefit an increased interest from scientists and engineers from various field due to their great potential and environmental safety. Babak Taheri and collaborators demonstrated that the use of graphene flakes on the sprayed scaffold boosts the power conversion efficiency (PCE) of small-area cells up to 17.5% that corresponds to an increase of more than 15% compared to standard cells [9] studies that are also sustained in [10-12].

Carbon nanoparticles are structures with remarkable properties, but they have some disadvantages when trying to use them in many materials or devices. These disadvantages are the cost of production and the possibility to integrate them into existing technologies. Multiwalled carbon nanotubes (MWCNT) are composed of an atomic structure of long tubular shape obtained by rolling the carbon sheet along an arbitrary axis just like tobacco leaves in a cigar. Yet, to be

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used at their highest potential their properties must be studied at microscopic level as single particles, not as bulks. The biggest problems occurring when trying to determine nanoparticle's parameters are dispersion and orientation. Dispersion can be improved by chemical methods such as coatings and functionalization, and by physical methods by thermal agitation and/or sonication. Yet the orientation problem remains, and it is crucial for optical properties. Thus, it can be a good idea to find a material that can be used as an organized environment and can induce this organization to the nanotubes.

Liquid crystals (LC), known for revolutionizing the display technology, represent great candidates for this job. Generally, they own a property which is currently exploited. This is represented by the existence of mesophases i. e. intermediary phases between two states of aggregation (eg from liquid properties to solid). This state is called liquid crystal. These states combine the order of the solid with the flow property of the liquid and vice versa. As shown in [13-18] carbon nanotubes present a tendency to align their long axis parallel to the molecular director of nematic liquid crystals, so LC-s are ordered structures and induce orders in carbon nanotubes.

The general idea is that carbon materials are promising, due to their physical properties, potentially reduced costs and low environmental harm. It is our purpose to improve the carbon-based materials by developing theoretical models for several parameters such as dielectric permittivity, conductivity, or mechanical strength. The procedure is quite like the one presented in [19] where it can be seen that every theory is laboratory tested and improved until a good agreement between them is found. The main advantage we can provide for nanomaterials is the flexible and ordered host medium i. e. the liquid crystals. Due to their tendency to align with nematic director, well dispersed graphene can be easily studied just as we did with other nanoparticles in previous research [19-22].

2. **Experimental set-up and method**

One of the most known and used property of liquid crystals is their ability to change the orientation when subjected to an external field. This property allows the user to control the optical properties of the sample by the applied field. Yet this can only be possible if the field intensity is higher than a limit called the Freedericksz transition threshold. We aim to study this parameter for several samples of liquid crystals with carbon nanoparticles (nanotubes and graphene) to check the improvements that can be achieved for each of them.

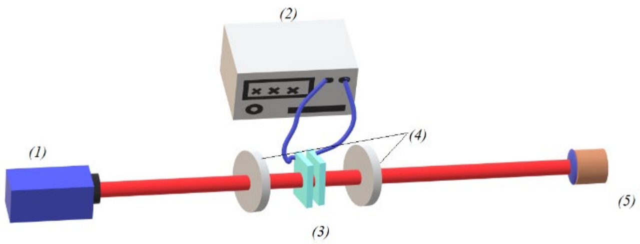


Fig. 1 Experimental set-up for the Freedericksz transition study: (1)-laser generator, (2)-power source to apply voltage on the sample, (3)-sample, (4)- crossed polarizers and (5)-photovoltaic cell

The set-up used for the Freedericksz transition threshold, is presented in Fig.1. A laser generator (1) sends a laser beam through the sample (3). The sample is subjected to a voltage by a power source (2) and placed between two crossed polarizers (4). Finally, the emergent beam is collected by a photovoltaic cell (5). The intensities were recorded manually or automatically for each sample and the Freedericksz transition voltage was evaluated from Intensity versus voltage plot.

The samples were made from 5CB liquid crystal composite with different carbon-based nanoparticles at very low concentrations which may help gaining a good dispersion. Mixture composition is given in Table 1. The mixtures were used to fill LC-cell from Instec with planar alignment and a 15 micrometers cell gap. The measurements were performed at a constant temperature of 26^{o} Celsius.

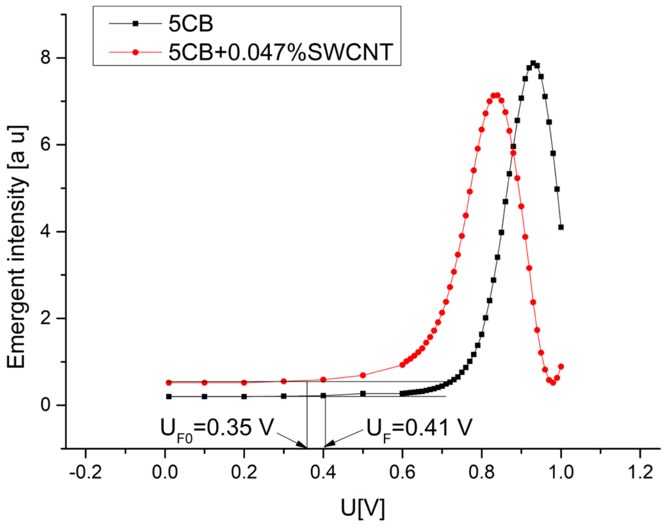
Table1

Mixture composition for the analyzed samples

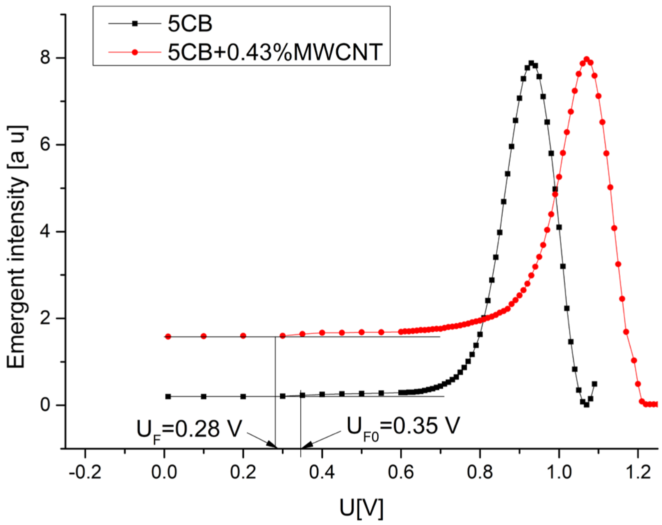
Sample name	Sample content	Concentration (mass fraction)
a	5CB	
b	5CB + SWCNT	0.047%
c	5CB + MWCNT	0.43%
d	5CB + graphene nanoplatelets	0.5%
e	5CB + (GQD)	0.5%

3. Results and discussion

The emergent intensity versus applied voltage plots recorded for each set of samples are presented in Fig.2. All the recordings were made at room temperature at few degrees above the solid-nematic transition. For each set the Freedericksz transition threshold (U_F) was determined as the point where the emergent intensity presents a slight variation (increase or decrease depending on the nematic director orientation). In the samples containing carbon nanoparticles, there are local disturbances of the molecular director induced by the anchoring process on the nanoparticle's surface. This reorientation changes the refractive index of the extraordinary ray and thus the initial emergent intensity is different from one sample to another. The obtained plots are shown in Fig. 2.



a)



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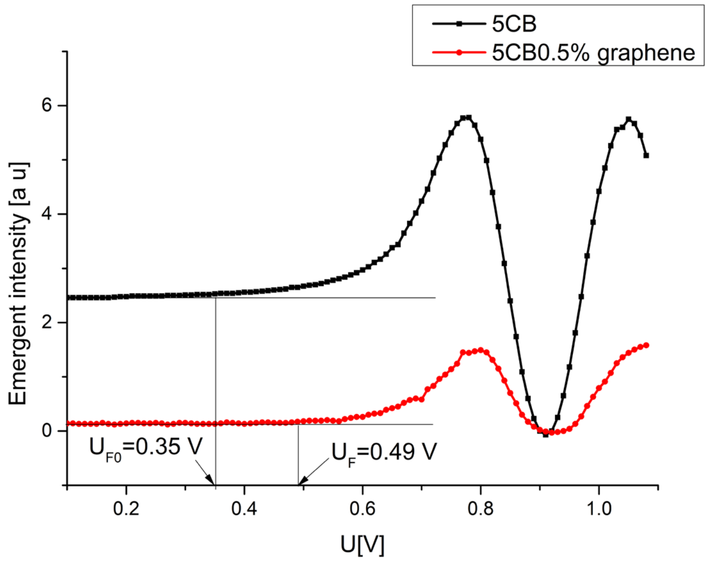
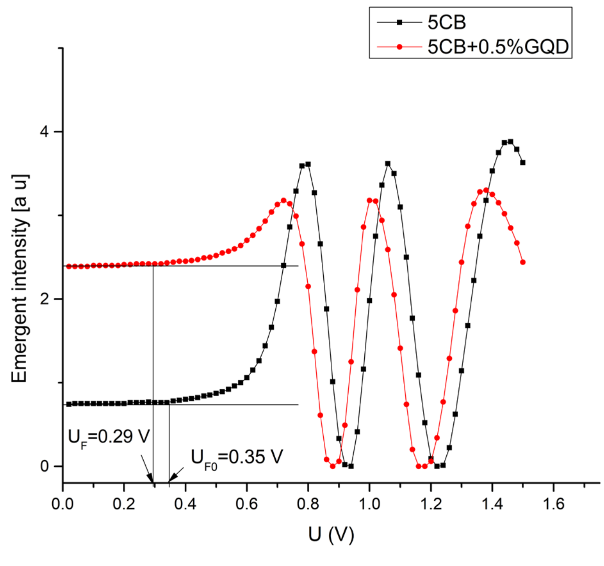


c)



d)

Fig. 2 Beam intensity versus applied voltage plots for a) 5CB, b) 5CB + SWCNT, c) 5CB + MWCNT, d) 5CB + graphene nanoplatelets, e)5CB + (GQD)

The transition threshold voltages were evaluated for each sample and the experimental values obtained are given in Table 2. From the results obtained in previous work performed on similar systems [1,17], we noticed that the Fredericksz transition of nematic composites with different nanoparticles leads to a multiplication factor $\sqrt{1-\kappa}$ depending on the anchoring angle of molecules on the nanoparticle's surface and on the nanoparticle electric property shape and clustering tendency:

$$U_F = \pi\sqrt{\frac{k_{11}}{\varepsilon_0 \Delta\varepsilon}}\sqrt{1-\kappa} \tag{1}$$

where

$$U_{0} = \pi\sqrt{\frac{k_{11}}{\varepsilon_0 \Delta\varepsilon}} \tag{2}$$

is the Freedericksz transition voltage of the pure nematic without any nanoparticles adding.

Using the experimental results, this amplification factor is determined and the results are presented in Table 2.

Table 2

Freedericksz transition threshold values for 5CB and its composites with carbon nanoparticles and the multiplication factor corresponding to each sample

Samples	U_{F0}[V]	U_F[V]	κ
5CB+0.047% SWCNT	0.35	0.41	0.27
5CB+0.43% MWCNT	0.35	0.28	-0.56
5CB+0.5%graphene nanoplatelets	0.35	0.49	0.49
5CB+0.5%GQD	0.35	0.29	-0.46

Generally, the value of k is negative for a homeotropic orientation of the molecules on the nanoparticle's surface and positive for planar anchoring [17,18] but the process is more complex and depends on particular properties of each nanoparticle. Furthermore, nanoparticle's clustering inside the sample leads to micrometric bulks and the molecules present a homeotropic anchoring on the bulk's surface.

As it can be observed from the experimental results, MWCNT (multiwalled carbon nanotubes) and GQD (graphene quantum dots) present an advantage for composites that can be used in LCD devices as they reduce the Freedericksz transition and thus, the power consumption increasing the lifetime of portable displays (cell phone, tablets, laptops etc). Furthermore, they don't have a significant influence on the emergent intensity. As it can be observed from Fig.3 the maximum intensity of GQD composite presents a slow decrease when compared to 5CB cell while the MWCNT has the same maximum intensity as 5CB. On the other hand, SWCNT (single-walled carbon nanotubes) and graphene nanoplatelets not only increase the Freedericksz transition but also absorb a lot of the incident radiation. Yet we must notice that they present a better dispersion than MWCNT so, with proper adjustments of concentration, they might present some advantages for LC-based device, but this research will be continued in the future.

4. Conclusions

Carbon based nanomaterials affect the electro-optic properties of LC-cell by changing the molecular orientation on certain regions inside the cell and thus, the Freedericksz transition threshold. The transition threshold (UF) can be decreased in certain cases by using the proper nanoparticles in very low concentrations. MWCNT and GQD reduce the UF values by 20% which is a great advantage in power consumption of LCDs.

R E F E R E N C E S

[1]. *Cristina Cirtoaje, Emil Petrescu, Cristina Stan, Andrey Rogachev* Electric Freedericksz transition in nematic liquid crystals with graphene quantum dot mixture 12th International Conference on Physics of Advanced Materials (ICPAM) Applied Surface Science Volume 487 Page 1301-1306DOI10.1016/j.apsusc.2019.05.073

[2]. *D.A. Petrov, and P.K. Skokov,* Ferromagnetic ordering theory of colloidal suspension of magnetic particles in liquid crystal Oct-dec 2020 | Liquid Crystals And Their Application 20 (4) , pp.63-71

[3]. *D. Manaila-Maximean, V. Cîrcu, P. Ganea, A. Bărar, O. Danila, T. Staicu, V.A. Loiko, A. Konkolovich, A.A. Miskevich,* 2018, December. Polymer dispersed liquid crystals films doped with carbon nanotubes: preparation methods. In Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies IX (Vol. 10977, p. 1097702). International Society for Optics and Photonics.

[4]. *V.A. Loiko, A.V. Konkolovich, A.A. Miskevich, D. Manaila-Maximean, O. Danila, V. Cîrcu, A. Bărar,* 2020. Optical model to describe coherent transmittance of polymer dispersed liquid crystal film doped with carbon nanotubes. Journal of Quantitative Spectroscopy and Radiative Transfer, 245, p.106892.

[5]. *Doina Manaila Maximean, Cristina Cirtoaje, Octavian Danila*, Novel Colloidal System: magnetite-polymer Particles/Lyotropic Liquid Crystal under Magnetic Field, April 2017 Journal of Magnetism and Magnetic Materials 438, DOI:10.1016/j.jmmm.2017.02.034

[6]. *Doina Manaila Maximean, Octavian Danila, Pedro L. Almeida Constantin Paul Ganea* Electrical properties of a liquid crystal dispersed in an electrospun cellulose acetate network January 2018 Beilstein Journal of Nanotechnology 9 DOI:10.3762/bjnano.9.18

[7]. *Petrescu, E; Bena, R.E. and Cirtoaje, C* Polarization gratings using ferronematics-An elastic continuum theory, Journal of Magnetism And Magnetic Materials 336 , pp.44-48

[8]. *AN Zakhlevnykh,; MS Lubnin, and DA Petrov,* A simple model of liquid-crystalline magnetic suspension of anisometric particles, 14th International Conference on Magnetic Fluids (ICMF) Jun 1 2017 | Journal of Magnetism And Magnetic Materials 431 , pp.62-65

[9]. *Babak Taheri, Narges Yaghoobi Nia, Antonio Agresti, Sara Pescetelli, Claudio Ciceroni, Antonio Esaù Del Rio Castillo, Lucio Cinà, Sebastiano Bellani, Francesco Bonaccorso, and Aldo Di Carlo*, Graphene-engineered automated sprayed mesoscopic structure for perovskite device scaling-up 2D MATERIALS, Volume 5, Number 4 https://doi.org/10.1088/2053-1583/aad983

[10]. *George Kakavelakis, Emmanuel Kymakis,Kostantinos Petridis*, 2D Materials Beyond Graphene for Metal Halide Perovskite Solar Cells, Advanced materials interfaces, volume 5, issue 22 https://doi.org/10.1002/admi.201800339

[11]. *Arora N, Dar M, Hinderhofer A3, Pellet N1, Schreiber F, Zakeeruddin SM, Grätzel M.* Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20% SCIENCE 358, 6364, p. 768 (2017); DOI: 10.1126/science.aam5655

[12]. *Abdulhadee Yakoh, Ruslan Álvarez-Diduk, Orawon Chailapakul*Arben Merkoçi* Screen-Printed Electroluminescent Lamp Modified with Graphene Oxide as a Sensing Device ACS Appl. Mater. Interfaces 2018, 10, 24, 20775–20782 https://doi.org/10.1021/acsami.8b04883

[13]. *V. Popa-Nita, S. Kralj,* 2010. Liquid crystal-carbon nanotubes mixtures, J. Chem. Physi. 132(2), 024902. https://doi.org/10.1063/1.3291078.

[14]. *P. Vander Schoot, V.Popa-Nita, S. Kralj,* Alignment of Carbon Nanotubes in Nematic Liquid Crystals, J. Phys. Chem. B 112 (2008) 4512-4518. https://doi.org/10.1021/jp712173n.

[15]. *M. H. Majles Ara, Z. Dehghani,* Improvement of the third order nonlinear optical properties of nematic liquid crystal under the influence of different compositional percentage of doped SWCNT and the external electric field, J. Mol. Liq. 275 (2019) 281-289. https://doi.org/10.1016/j.molliq.2018.11.069.

[16]. *C. Chang, Y. Zhao, Y. Liu, L. An,* Liquid crystallinity of carbon nanotubes, RSC Advances, 8(28) (2018) 15780-15795. https://doi.org/10.1039/c8ra00879e..

[17]. *S.P. Yadav, S. Singh,* Carbon nanotube dispersion in nematic liquid crystals: An overview Prog. Mater. Sci. 80 (2016) 38-76, https://doi.org/10.1016/j.pmatsci.2015.12.002.

[18]. *I. Dierking, G. Scalia, P.* Morales Liquid crystal–carbon nanotube dispersions JOURNAL OF APPLIED PHYSICS 97, 044309 s2005d, https://doi.org/10.1063/1.1850606

[19]. C. Cirtoaje, E. Petrescu, and V. Stoian, Electrical Freedericksz transitions in nematic liquid crystals containing ferroelectric nanoparticles PHYSICA E-LOW-DIMENSIONAL SYSTEMS & NANOSTRUCTURES 67 , pp.23-27

[20]. *D.A. Petrov, A.N. Zakhlevnykh, A.V. Mantsurov,* Orientational Ordering of a Liquid-Crystal Suspension of Carbon Nanotubes in a Magnetic Field, J. Exp. Theor. Phys. 127(2)(2018)357-369. doi:10.1134/S106377611808023X.

[21]. *A. N. Zakhlevnykh, D. A. Petrov, P. K. Skokov,* Influence of Ferromagnetic Carbon Nanotubes on Magnetic Transitions in Liquid Crystals, J. Exp. Theor. Phys., 127(4)(2018)767-777, doi:10.1134/S1063776118090236.

[22]. *Burylov, S. V., Zakhlevnykh, A. N.,* Orientational energy of anisometric particles in liquid-crystalline suspensions, Phys. Rev. E 88, 012511. https://doi.org/10.1103/PhysRevE.88.012511