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Measurement of magnetic anisotropy of multiwalled carbon nanotubes in nematic host

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HIGHLIGHTS

- A study MWCNTs dispersion in nematic liquid crystals was performed.
- A theoretical model for NLC–MWCNT interaction was developed.
- A new method for the measurement of magnetic anisotropy of MWCNT was proposed.
- Reliable and reproducible were obtained.

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ABSTRACT

The magnetic anisotropy of multiwalled carbon nanotubes (MWCNT-s) is measured using their dispersion in nematic liquid crystal (NLC). Due to their ability to align themselves with inserted nano-particles, NLC are very useful for the study of the physical properties of MWCNT as well as for other micro or nano-particles. Thus an organized system is obtained from the beginning and the influence of initial random orientation is considerably reduced. The average magnetic anisotropy of MWCNT dispersed in NLC was calculated from the system relaxation time and the obtained value (6.61×10^{-5}) was in good agreement with other reported results.

1. Introduction

Discovered by Iijima [1] in 1991, carbon nanotubes (CNT-s) are widely used in various fields such as engineering, science, environmental protection or medicine due to their unique properties. Many studies revealed their importance in electro-optical devices [2,3], in waste water cleaning from a wide variety of pollutants [4,5] or in some medical devices as they proved to have antibacterial properties [6,7]. All these results encouraged the scientists not only to develop new chemical synthesis methods but also to improve their properties by functionalization or other chemical or physical procedures [10]. Since the physical properties of micro- or nano-particles are different from the bulk properties of the same substance, the researchers must find new methods to organize these particles in relatively stable systems that can be easily and efficiently studied. A proper organization can be reached by inserting them in NLC [8,9]. There have been developed many devices based on NLC with inserted dyes, micro-particles or nano-particles. These mixtures can be used for the study of particle's physical properties as well as in engineering to improve existing devices or to develop new ones [10–19]. The liquid crystals, mainly used in LCD's, combine the properties of crystalline structure of solid state with those of liquid phase, leading to an organized movement of inserted to CNT-s. Theoretical and experimental studies performed on CNT-NLC mixtures from the orientation, elastic, optic or magnetic properties point of view [20,21] helped us to develop a new procedure for the measurement of MWCNT magnetic anisotropy. This method can also be applied for any other rod – like nano- or micro-particles by taking advantage of nematic molecules orientational abilities.

Since CNT were discovered, their magnetic properties were studied in many theoretical or experimental ways [22–25] but they all have to face the inconvenience of clustering and disordered orientation that must be compensated by the magnetic field. Previous results [22–25] showed that carbon nanotubes are diamagnetic both on parallel and perpendicular orientation to their axis but the magnetic susceptibility $\chi_\perp$ is larger than $\chi_\parallel$ resulting a paramagnetic overall behavior and a reorientation of carbon nanotubes parallel to the applied field. This makes them easy to be

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used in thermotropic liquid crystals also which have positive anisotropy.

2. Theoretical background

When a nematic liquid crystal (NLC) is subjected to an external field higher than critical Freedericksz transition threshold, a reorientation of molecular director is induced leading to a birefringence variation. Thus when the LC is subjected to a laser beam a succession of maxima and minima of the transmitted light through the sample appears. The order number N of intensity minima can be expressed as a function of the maximum deviation angle θ_m [26]

$$N = \frac{d\Delta n}{2\lambda}\left(\theta_m^2 - \frac{\theta_m^4}{4}\right)$$

where d is the cell thickness and λ is laser wavelength.

The maximum deviation angle can be calculated (for nematic LC) using elastic continuum theory of liquid crystals. This theory is based on the evaluation of the system's free energy density considering all the interactions between the system's components: LC molecule – MWCNT, LC molecule–external field and MWCNT–external field.

Assuming a parallel orientation of carbon nanotubes to nematic molecules [5,27] and an interaction process based on Burylov's model [28] we can evaluate the LC molecule – MWCNT interaction energy density

$$f = \frac{wc}{2R}\left(1 - 3\cos^2\alpha\right)\left(\vec{u}\,\vec{n}_0\right)^2 = \tilde{w}\left(\vec{u}\,\vec{n}_0\right)^2 \tag{1}$$

which can be written in a simplified form

$$f = \tilde{w}\left(\vec{u}\,\vec{n}_0\right)^2$$

where

$$\tilde{w} = \frac{wc}{2R}\left(1 - 3\cos^2\alpha\right),$$

α is the anchoring angle of nematic molecule on the MWCNT, w is the anchoring energy, $\vec{u}$ is the molecular orientation of the MWCNT, $\vec{n}_0$ is the unperturbed nematic director, c is the volumetric concentration of nanotubes and R is the MWCNT radius (Fig. 1).

When an external field is applied perpendicular to the undisturbed nematic director (Fig. 2a) both the LC molecules and carbon nanaotubes tend to align themselves parallel to the field direction due to their positive magnetic anisotropy. A detailed

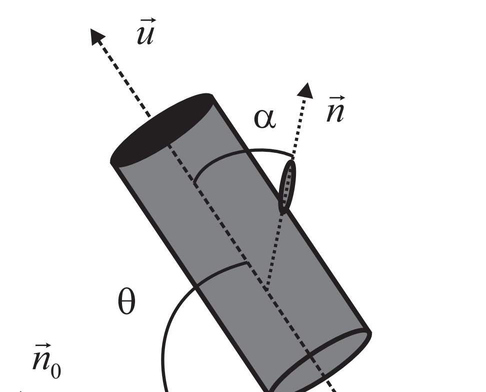

Fig. 1. Molecular orientation of the nematic molecule on the nanotubes's surface.

descrition of this reorientational process made in a similar system is given in [29]. The system's free energy density is the sum of the density energies describing all the interactions mentioned above

$$f = f_{NLC} + f_{MLC} + f_{MWCNT} + f_{int} + f_{\gamma} \tag{2}$$

- f_{NLC} – the elastic term, characterizing elastic deformation of the NLC

1. f_{MCL} – the influence of the applied magnetic field on the NLC reorientation
2. f_{MWCNT} – the magnetic field action on MWCNT
3. f_{int} – the NLC–MWCNT interaction term
4. f_{γ} – the rotational viscosity term

Each of these energy densities can be written in mathematical terms as it follows:

$$f_{NLC} = \frac{1}{2}\left[K_1\cos^2\theta + K_3\sin^2\theta\right]\left(\frac{\partial\theta}{\partial z}\right)^2 \tag{3}$$

where K_1 and K_3 are splay and bend elastic constants,

$$f_{MCL} = -\frac{1}{2}\mu_0^{-1}\chi_a B^2\sin^2\theta \tag{4}$$

where χ_a is NLC's magnetic anisotropy,

$$f_{MWCNT} = -\frac{1}{2}\mu_0^{-1}\chi_{aN} cB^2\sin^2\beta \tag{5}$$

where χ_{aN} is MWCNT's magnetic anisotropy,

$$f_{int} = \tilde{w}\cos^2\left(\theta - \beta\right) \tag{6}$$

where θ is NLC's deviation angle and β is MWCNT's deviation angle in magnetic field (Fig. 2a), and

$$f_{\gamma} = -\frac{1}{2}\gamma\left(\frac{\partial\theta}{\partial t}\right) \tag{7}$$

where γ is the rotational viscosity coefficient. The total free energy is

$$F_T = \int_{-d/2}^{d/2} f(z)dz \tag{8}$$

By applying Euler–Lagrange equations to the function described in Eq. (8), using small angles approximation, we obtain:

$$\beta = \frac{2\tilde{w}\theta}{2\tilde{w} - \mu_0^{-1}c\chi_{aN}B^2} \tag{9}$$

and

$$\left[K_1\left(\theta^2 - 1\right) - K_3\theta^2\right]\frac{\partial^2\theta}{\partial z^2} + \left(\theta - \frac{2\theta^3}{3}\right)\left(K_1 - K_3\right)\left(\frac{\partial\theta}{\partial z}\right)^2 - A\theta + D\frac{2\theta^3}{3} = -\gamma\frac{\partial\theta}{\partial z} \tag{10}$$

where by A and D we denoted

$$A = 2\tilde{w}\left(\frac{-\mu_0^{-1}c\chi_{aN}B^2}{2\tilde{w} - \mu_0^{-1}c\chi_{aN}B^2}\right) + \mu_0^{-1}\chi_a B^2$$

and

$$D = 2\tilde{w}\left(\frac{\mu_0^{-1}c\chi_{aN}B^2}{2\tilde{w} - \mu_0^{-1}c\chi_{aN}B^2}\right)^3 + \mu_0^{-1}\chi_a B^2$$

The deviation angle θ does not have a constant value on the whole cell thickness due to the anchoring effects of NLC molecules