ENHANCED PHYSICAL PROPERTIES OF NEMATICS DOPED WITH FERROELECTRIC NANOPARTICLES

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Abstract - We show experimentally and theoretically that ferroelectric nanoparticles could produce enhanced changes in the physical properties of a liquid crystal (LC) host. It is introduced how to use the ferroelectric nanoparticles for the preparation of various LC-ferroelectric nanoparticle composites. In the process we also present how to prepare these composites using other ferroelectric nanoparticles as well as to improve the physical properties of the host LC. Following the preparation of LC-particle composites, we present experimental data obtained that compares differences between nanoparticle (ferroelectric) doped LC host and unmodified LC. We review a few key points related to how we selected a single component LC to provide various methods of enhancing the physical properties of host LC and the mixed results we obtained when we worked with commercial LC mixtures.

Key words: nematic liquid crystals, ferroelectric nanoparticles

1. Introduction

Nematic liquid crystals (NLCs) are very sensitive to the presence of nanoparticles. This property explains the fact that NLCs rapidly become key technological materials for such applications as, for example, information displays. NLCs are also in the focus of intense interdisciplinary investigations as systems with reach supramolecular structures. In recent years there has been continuously growing interest in physical effects caused by addition of ferroelectric nanoparticles to LCs [1–6]. These dispersions are stable at low concentrations (less than 0.1-1 weight percent). An important point is that the nanoparticles are so small that the anchoring parameter $\xi = WR/K \ll 1$ (here W is the anchoring energy, K is the elastic constant, R is the characteristic size of the particles). At this small size the nanoparticles do not substantially disturb the orientation of the LC director [7] and therefore produce a macroscopically uniform alignment. As a result, the ferroelectric dispersion appears similar to a pure LC with no readily apparent evidence of dissolved particles. The nanoparticles produce substantial changes in the physical properties of the LC host – they enhance the order parameter, birefringence, and dielectric anisotropy [2, 8]. The nanoparticles share their intrinsic properties with the medium they are dispersed in.

However, whether particles retain their ferroelectricity or not after dispersing into a LC host is an interesting piece of information that helps us to understand these composites and is not yet well studied. In the literature, at the time of this research it had not been demonstrated that dispersed ferroelectric nanoparticles would still retain their ferroelectricity during the preparation process and maintain it in the final LC-ferroelectric nanoparticle composite. We demonstrate that indeed these composites do retain the macroscopic ferroelectric properties after dispersing them into the host LC. Probably, these results, first time, confirm the various enhancements in the physical properties of particle dispersed LC host are the direct result of ferroelectricity of the dispersed nanoparticles into a single component stable LC 4-n-pentyl-4'-cyanobiphenyl (5CB).

In this paper we observed and studied the increase of the clearing temperature, T_{NI} , dielectric anisotropy, ε_a , and birefringence, n_a , of the ferroelectric nanoparticles doped in NLC. We

propose a new theory for the statistical mechanics of ferroelectric nanoparticles in liquid crystals, which is based specifically on the orientational distribution of the nanoparticle dipole moments. This distribution is characterized by an orientational order parameter, which interacts with the orientational order of the liquid crystals and stabilizes the nematic phase. We estimate the coupling strength and calculate the resulting enhancement in T_{NI} , in good agreement with experiments. This enhancement occurs even when electrostatic interactions are partially screened by moderate concentrations of ions in the liquid crystal.

2. Statistical mechanics of ferroelectric nanoparticles in LC

In calculations we assume that nanoparticles are spheres with radius R, electric moment \mathbf{p} and are surrounded by NLC molecules. The electric field E generated by the nanoparticle interacts with the order tensor Q_{ij} of the liquid crystal through the free energy

$$F_{\rm int} = -\frac{\varepsilon_a}{12\pi} \int d^3 r Q_{ij} E_i(\mathbf{r}) E_j(\mathbf{r}), \qquad (1)$$

where ε_a is the dielectric anisotropy of the fully aligned LC. The electric field of the nanoparticle has a standard dipolar form

$$\mathbf{E} = \frac{1}{\varepsilon} \left(\frac{3\mathbf{r} \left(\mathbf{r} \mathbf{p} \right)}{r^5} - \frac{\mathbf{p}}{r^3} \right).$$
(2)

Here ε is average dielectric permittivity of NLC and we neglected higher-order corrections due to the dielectric anisotropy of the NLC. Following to [9], we can write free energy of ferroelectric nanoparticles doped in NLC in the form

$$F = \frac{a_{LC}}{2} \left[T - T^* - \frac{\rho_n^2}{a_{LC}a_n} \left(\frac{\varepsilon_a p^2}{45\varepsilon^2 R^3} \right)^2 \right] S_{LC}^2 - \frac{b}{3} S_{LC}^3 + \frac{c}{4} S_{LC}^4,$$
(3)

where a_{LC} is the leading coefficient in the Landau-de Gennes representation of NLC free energy and can be estimated through Maier-Saupe theory as $a_{LC} = 5k_B\rho_{LC}$, ρ_{LC} is the concentration of LC molecules per volume, T^* is the temperature, below which the isotropic phase of pure NLC is completely unstable with respect to nematic ordering, ρ_n is the nanoparticles concentration per volume, a_n is the leading coefficient of nanoparticles part of free energy and can be estimated through Maier-Saupe theory as $a_n = 5k_B T \rho_n$ and S_{LC} is the scalar order parameter of NLC.

Now from (3) we can get the scalar order parameter and phase transition temperature change of NLC doped with ferroelectric nanoparticles

$$\Delta T_{NI} = \frac{\rho_n^2}{a_{LC}a_n} \left(\frac{\varepsilon_a p^2}{45\varepsilon^2 R^3}\right)^2 = \frac{\varphi_n \pi^3 R^3}{3T_{NI}\rho_{LC}} \left(\frac{8\varepsilon_a P^2}{675k_B \varepsilon^2}\right)^2,\tag{4}$$

$$S_{LC} = (2c)^{-1} \left[b + \sqrt{b^2 - 20k_B \rho_{LC} c \left(T - T^* - \Delta T_{NI} \right)} \right].$$
(5)

The last expressions can be simplified by writing

$$p = \left(\frac{4}{3}\pi R^3\right)P, \qquad \rho_n = \varphi_n / \left(\frac{4}{3}\pi R^3\right), \qquad (6)$$

where *P* is polarization per volume and ϕ_n the volume fraction of the nanoparticles. For calculations we use the following parameters appropriate for Sn₂P₂S₆ nanoparticles in the NLC 5CB: $\phi_n = 0.5\%$, R = 35nm, $T_{NI} = 308K$, $\rho_{LC} = 2.4 \times 10^{21}$ cm⁻³, $P = 10^4$ CGSE = 0.04 Cm⁻², $k_B = 1.38 \times 10^{-16}$ erg/K, $\varepsilon_a = 13.3$, $\varepsilon = 6.7$ [9]. With these parameters, we obtain $\Delta T_{NI} \approx 5$ K, which is roughly consistent with the increase that is observed experimentally. Of course, there is a substantial uncertainty in this estimate, because the parameters *R* and *P* are not known very precisely in the experiments.

3. Preparation of LC-particle composites

The commercial ferroelectric nanopowders are usually the main ingredients for making ferroelectric ceramic materials. They are pulverized from large crystal and sieved to a nominal size range. Most of these particles lose their polarization due to strong mechanical collisions during a milling process. If there is any polarization remaining, their strong dipolar moment can induce severe aggregation at the μ m scale. Some of the post treatments such as sintering at high temperature (>1000 °C) help to restore the polarization lost during the pulverization process. However, these processes often require high voltage (>kV) poling. These treatments are difficult to apply to LC-particle composites, as we have not found reliable and repeatable processes to coat ferroelectric particles with a precise amount of surfactant. In addition, we cannot find submicron size and reliable ferroelectric particles.

The particle suspension is mixed with LC usually within hours after production to reduce any possible chance of aggregation. However, we later found that the particle suspensions are stable for months after their preparation. The preparation of LC-particle composites involves dispersing ferroelectric particle suspensions into a LC host. Prior to dispersing particle mixtures into the LC host, the total particle concentration in the carrier liquid (solvent) is measured. Often 0.5 to 1.5 grams of a pre-calculated amount of particle suspension is mixed with the LC host in order to achieve less than 0.1 - 1 final weight percent of ferroelectric particles dispersed in LC host. The carrier liquid is removed from the LC mixture by heating the mixture just above the evaporating temperature of carrier liquid, while the mixture is stirred at a uniform speed. The process is continued until no variation in the total weight of the resultant LC-particle composite is observed.

Finally, the LC-particle composite is microscopically inspected for the presence of defect structures. We observe no evidence of dispersed colloidal particles in the LC host when examining the composites under a standard polarizing microscope. These mixtures resemble pure LC under all optical microscope observations.

As we selected and studied the single component LC 5CB as the host, any changes in the properties of 5CB must be the direct result of the added particle properties. In the present work, we focused on samples where the influence of the ferroelectric particles is unambiguous. We have focused on samples where T_{NI} has increased as a direct effect of the ferroelectric nanoparticles. We use three types of particle suspensions; each obtained from a variety of fabrication methods [1, 10–12]. Ferroelectric nanoparticle colloids are briefly described here:

1) LC-particle composite fabricated from high energy ball mill (HEBM) processed 3μ m BaTiO₃. The process of obtaining these particles presented in [10, 11]; 2) LC-particle composite fabricated from 50 nm BaTiO₃ particles using nonhydrolytic route/open bench method [12]; 3) LC-particle composite fabricated from Sn₂P₂S₆ particles using noncommercial simple mill process [1].

As we show below, we find an increase in clearing temperature T_{NI} and improved physical properties of various 5CB dispersions using ferroelectric $Sn_2P_2S_6$ and $BaTiO_3$ ferroelectric particles.

4. Experimental study

We measured the scalar order parameter (S_{LC}) and other physical properties of various ferroelectric nanoparticle dispersed LC composites. These composites include the three samples we mentioned above that unambiguously showed enhancements in their physical properties and other composites that lack any enhancements we expected to observe. One of the main reasons why we could not see the enhanced physical properties in the LC-particle composite is the control of surfactant. We present the order parameter and differential scanning calorimetric (DSC) measurements of these composites. Later we show the direct presence of ferroelectricity after dispersing the particles in the LC host followed by in-plane switching (IPS) measurements showing their high stability.

We used crystals of tin thiohypodiphosphate ($Sn_2P_2S_6$) to produce ferroelectric nanoparticles or high energy ball milled ferroelectric barium titanate (BaTiO₃) particles. Before proceeding to our experimental procedures, let us briefly present the basics of $Sn_2P_2S_6$ particles. At room temperature, macroscopic $Sn_2P_2S_6$ crystals have a spontaneous polarization of 14μ C cm⁻² parallel to the direction of the monoclinic cell [13]. The Curie temperature of $Sn_2P_2S_6$ in a macroscopic crystal is $T_{Curie} \approx 66^{\circ}$ C [14]. The value of the dielectric constant of $Sn_2P_2S_6$ along the main axis, ε_{\parallel} , strongly depends on the quality of the samples [15]. Typically, $\varepsilon_{\parallel} \approx 300$ in a single domain crystal and is about twice as large as in a polydomain state due to the domain wall contribution to the dielectric permittivity, experimental studies of which have also been reported for $Sn_2P_2S_6$ [15].

Micro-particles of $Sn_2P_2S_6$ are ground together with oleic acid as a surfactant in a vibration micro-mill for 120 hours. Atomic force microscopy showed that the upper size limit of the particles is 70 nm [16]. The mixture of the nanoparticles with the surfactant is dispersed in the nematic 5CB (clearing temperature, $T_{NI} = 34.5^{\circ}$ C) using an ultrasonic mixer. The nematic dispersion has a volume fraction of particles $\varphi_n \approx 0.2$ volume percent. We prepared several dispersions using the identical procedure and conditions (temperature, humidity, milling time, etc.). We prepared the dispersions using $Sn_2P_2S_6$ or $BaTiO_3$ colloids from the same batch as well as from different batches.

The substrates are covered with rubbed polyimide polymer layers to produce uniform homogenous alignment. The dispersions are studied in cells comprised of two ITO coated glass substrates. The substrates are separated by rod-shaped glass-spacers and we obtained a 5.0 μ m (±0.2 μ m) cell gap, verified using spectrophotometry.

The cells are capillary filled at elevated temperature, $T >> T_{NI}$. Observations of all samples in a polarizing microscope showed the same uniform planar textures in the cells filled with the pure nematic and with the dispersion. The dispersions in the cells are stable for at least several months; we did not find any visible aggregations of the particles by optical microscope observations. We think that, besides the surfactant coating, the high stability of the dispersion results from the orientational elasticity of the mesophase. If the particles agglomerate, their effective size increases and, at some point, requires the creation of high-energy defects. This will prevent aggregation and maintain the dispersion as single particles or agglomerations with dimensions below the threshold requiring formation of a defect. Once the LC-particle composite is stable, we measured their order parameter, clearing temperature and dielectric anisotropy.

In order to measure the order parameter of the LC-particle mixture, we measured the dichroism, followed by measuring the clearing temperature and dielectric anisotropy of various LC-particle composites. We used dichroism measurements to measure the order parameter of various LC-particle composites.

The LC-particle composite is filled into a NaCl cell treated with homogeneously aligned rubbed polyimide layer. We measure the dichroism of the stretch vibration $C\equiv N$ bond. This group is selected since the long axis of the LC molecule is oriented in the same direction. Various dichroism measurements are obtained using a Nicolet-550 FTIR spectrometer. Consider A_{\parallel} and A_{\perp} as the dichroism of LC absorbance along and perpendicular to the polarization of the wire-grid polarizers used. During these measurements, the device is placed on a hot stage for temperature dependent studies of the order parameter.

We measured the average order parameter of the dispersion, S_d , and the pure LC, S_{5CB} , as a function of temperature using the guest-dye technique [17]. We used Methyl Red (MR) as the guest dye. In the guest-dye technique the order parameter is determined from the optical density of the probe dye molecules' absorption measured for light polarization parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the LC director orientation:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}.$$
(7)

Strictly speaking, this method does not give the value of the order parameter of a LC, S_{5CB} , but the order parameter of the dye molecules' orientation, S_{dye} . However, in the nematic phase, the comparison of the values, obtained in our experiments with the values obtained by NMR technique in [18] shows a difference of only 3%. Therefore, we consider that $S_{5CB} \approx S_{dye}$.

Our measurements showed varying positive changes in S. The variations in S ranged from 10% to 20% depending on the LC-particle mixture used for the measurement. The typical temperature dependence of the order parameter of unmodified 5CB and the three dispersions are presented in Figure.



Figure. Increase in the order parameter of various 5CB-ferroelectric nanoparticle composites.

In the samples made with BaTiO₃ particles of 11nm and 50nm, we observed a clear increase of the average order parameter in the dispersion and an increase of the clearing temperature, $\Delta T_{NI} = T_{NI,disp} - T_{NI,5CB} \approx +4.5$ and 2.5 °C respectively.

In the samples made with $Sn_2P_2S_6$ particles in the same particle size range (11nm), we observed the increase in the clearing temperature $\Delta T_{NI} = T_{NI,disp} - T_{NI,5CB} \approx +4$ °C and an average increase in order parameter in the dispersion.

A sample made using the same composition and procedures as the above samples has a lower order parameter and a decrease of the clearing temperature, $\Delta T_{NI} \approx -2^{\circ}C$. In fact, more samples are irreproducible than reproducible with the enhanced physical parameters. We shall look into various factors and optimizing reproducibility conditions later.

5. Conclusions

We used a number of LC-particle composites that used either $BaTiO_3$ or $Sn_2P_2S_6$ ferroelectric nanoparticles. Despite identical fabrication procedures in some cells we observed an increase of the average order parameter and clearing temperature of the LC, while in others, we observed no

change or a decrease. Positive and negative changes in the order parameter and T_{NI} are observed not only in the dispersions made from the $Sn_2P_2S_6$ or $BaTiO_3$ particle colloids from different batches, but in the dispersions of the same batch.

We first compared the clearing points, T_{NI} , in the unmodified 5CB and in the 5CB LCparticle composite. We determined the variations in the clearing point, T_{NI} of these composites by repeated DSC measurements. In the process, LC-particle composites undergo a 0.5° C/min temperature ramp up and ramp down multiple number of times. For positively enhanced LCparticle composites, we observed shifts in the clearing temperature ($\Delta T_{NI} = T_{NI,disp} - T_{NI,5CB}$), which ranged from +0.1 to 4.5°C.

However, we considered many factors could affect the physical properties of the LC host, 5CB. When preparing the LC-particle composite, for example, the clearing temperature may be lowered by residual free oleic acid. Also, non-ferroelectric particles may be expected to lower the clearing point and change other macroscopic properties. To continue our studies, we focused on studying the dispersions where the unique effects of ferroelectric particles are unambiguous, such as increase in T_{NI} of 5CB, and an associated introduction of ferroelectric behavior into the nematic LC 5CB.

According to Li and others [2], the electric field induced by the polarized nanoparticle enhances the orientation coupling in a LC host and leads to the increase of the clearing point, ΔT_{NI} . This increase is related to a permanent polarization of the ferroelectric nanoparticles by the formula (4). We have to note that actual value of *P* in (4) must be much lower as compared with the polarization of macroscopic crystals because the permanent intrinsic polarization of the particles may be partially screened by charged ions that are always present in a LC. However, we cannot provide an immediate order of magnitude estimate. The oleic acid surfactant can also screen the polarization of the particles. It is possible that the decrease of the clearing point may result from either a complete screening of the permanent polarization of the particles or by the loss of the ferroelectricity of the particles during the preparation of the dispersion.

For the case when $\Delta T_{NI} < 0$, currently we can suggest that due to unknown factors such as excess oleic acid or presence of low or no ferroelectricity, etc., the permanent polarization of ferroelectric particles could be screened by external charges or may be completely absent. It seems reasonable that the duration of the grinding time, and the conditions during the growing of the original Sn₂P₂S₆ crystals may result in dispersed particles of different shape and size [10], and that their spontaneous polarization may vary. The contamination of the experimental cells with ions may vary for different samples. The electric field produced by the spontaneous polarization of the particles will increase the order parameter of LC molecules. Alternatively the interaction and anchoring of LC molecules at the particle surface and the adsorbed surfactant [10] molecules may increase or decrease the order parameter of the LC molecules, depending on the strength of this interaction. Cordoyiannis et al. [19] recently confirmed this possibility, where strong impact of the surface coating of ferromagnetic nanoparticles to the isotropic-to-nematic transition is observed. The net effect of all the above factors may be an increase or decrease of the order parameter of the LC molecules, and may result in a corresponding change of the clearing temperature.

We found that even < 0.5 weight percent of oleic acid dissolved in LC, decreases the clearing temperature by $\Delta T_{NI} \approx -2.7^{\circ}$ C. The presence of free oleic acid in the LC bulk will act as a non-mesogenic impurity and lowers T_{NI} . These results are comparable with the characteristic value of the negative shift of T_{NI} in the dispersion. It suggests that this factor alone could explain the negative component of the clearing temperature shift. Undoubtedly a precise controlling of the amount of OA and converting all of it into bound-surfactant on the ferroelectric nanoparticles could be one of the most significant impediments to clarifying the research and achieving repeatable results. We provide some suggestions that are not directly related to surfactant.

Today we know how to synthesize colloidal particles using ball milling and other processes and improve physical properties of LCs by mixing them, respectively. However, many aspects of controlling the physical properties are not yet clear. Particle size and consistent preparation of colloidal particles are a few of the key factors. We learned one key factor is optimizing the amount of free oleic acid present in the LC-particle composite. We wanted to understand and produce ferroelectric colloids with a precise amount of surfactant coated for a given particle size. In next chapter we focus on how to just achieve it and minimize the surfactant coating on the ferroelectric nanoparticle colloids and estimate the necessary amount of surfactant necessary for a given particle size.

In conclusion, we observed and reported that ferroelectric nanoparticles dispersed into the single-component LC behave as a molecular dipole and can either increase or, in some cases, decrease the resulting order parameter of the LC mixture. In the first case, it results in a corresponding increase of the clearing temperature, T_{NI} , dielectric anisotropy, ε_a , and birefringence, n_a , of the dispersion, i.e., the particles can behave as a mesogenic molecular dopant to a mesogenic LC host, 5CB. In addition, in-plane switching experiments of various composites with increased T_{NI} demonstrated a way to break the particle dipole symmetry and coupling between particle dipole and LC host by observing a change in the resulting birefringence. IPS measurements also help to check the presence of ferroelectricity in the LC-particle composites. However, in the second case the particles behave as non-mesogenic molecular impurities, by decreasing or not exhibiting any effect the values T_{NI} , ε_a and n_a . The results clearly show that the primary mechanism of the influence of nanoparticles on the properties of single-component LC is a change of the orientation coupling in a LC host.

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