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Yurii Reznikov
Institute of Physics, Ukraine

Olexander Buchnev
Institute of Physics, Ukraine

Olexander Tereshchenko
Institute of Physics, Ukraine

Victor Reshetnyak
Kyiv Taras Shevchenko University

Anatoliy Glushchenko
Kent State University - Kent Campus

See next page for additional authors

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Authors

Yurii Reznikov, Olexander Buchnev, Olexander Tereshchenko, Victor Reshetnyak, Anatoliy Glushchenko, and John L. West

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Ferroelectric nematic suspension

Yurii Reznikov, Olexander Buchnev, and Olexander Tereshchenko
Institute of Physics, Pr. Nauki 46, Kyiv 03039, Ukraine

Victor Reshetnyak
Kyiv Taras Shevchenko University, Pr. Glushkova 6, Kyiv 03680, Ukraine

Anatoliy Glushchenko and John West[a]
Kent State University, Liquid-Crystal Institute, Kent, Ohio 44242

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We report on the development of a dilute suspension of ferroelectric particles in a nematic liquid-crystal (LC) host. We found that the submicron particles do not disturb the LC alignment and the suspension macroscopically appears similar to a pure LC with no readily apparent evidence of dissolved particles. The suspension possesses enhanced dielectric anisotropy, and is sensitive to the sign of an applied electric field.
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Long-range forces between ultrafine particles embedded in liquid-crystal (LC) matrices produce intriguing colloids.[1–10] For example, dispersed ferromagnetic particles greatly enhance the magnetic properties of the LC.[1–5] Large ($\gg\mu$m) colloidal particles form defects in LC matrices producing large director deformations. Ensembles of these particles and defects can form complex structures.[6–8] High concentrations ($>2\%$–3% by weight) of submicron particles can create almost rigid LC suspensions.[9,10] Here, we show that at low concentrations, LC colloids behave as a pure LC with no evidence of dissolved particles, but have enhanced properties. These dilute suspensions are stable because the nanoparticles do not significantly perturb the director field in the LC, and interaction between the particles is weak. Importantly, the nanoparticles share their intrinsic properties with the LC matrix due to the alignment with the LC. In particular, doping a nematic LC matrix with ferroelectric nanoparticles produces enhanced dielectric anisotropy and introduces the ferroelectric properties inherent to the nanoparticles.

We used particles of the ferroelectric thiohypodiphosphate ($Sn_2P_2S_6$) for the suspension. At room temperature, $Sn_2P_2S_6$ has a spontaneous polarization of 14 $\mu C\,cm^{-2}$ parallel to the [101] direction of the monoclinic cell.[11] The value of the dielectric constant of the $Sn_2P_2S_6$ along the main axis strongly depends on the quality of the samples and varies from 200 for ceramic samples to 9000 for monodomain crystals.[12] We selected $Sn_2P_2S_6$ for its low Curie temperature, $T_{\text{Curie}}\approx 66\,°C$, which is below the clearing temperature, T_c, of many nematic LC mixtures. For example, we used the nematic LC mixture ZLI-4801 (Merck) having a $T_c = 93\,°C$, and a low dielectric anisotropy ($\varepsilon_a^{ZLI}=3.2$), highlighting the contribution from the ferroparticles. In some experiments, we used a model nematic LC 5CB.

We obtained small ferroelectric particles by milling large particles ($\cong 1$ μm size) as opposed to chemical fabrication because milling can be used to produce smaller (10 nm) ferroelectric particles.[13] The resulting ferroelectric particles were mixed with a solution of oleic acid (surfactant) in heptane in a weight ratio of 1:2:10, respectively. The particles were ultrasonically dispersed and ground in a vibration mill for 120 h. The resulting ferroelectric particle suspension was mixed with the LC. The heptane was then evaporated and the mixture was ultrasonically dispersed for 5 min. The relative concentrations of components were adjusted to give a final suspension with about 0.3% by volume of ferroparticles.

Planar cells were filled with the LC suspension or pure LC at an elevated temperature $T > T_c$. The cells consisted of two indium tin oxide (ITO) coated glass substrates with a rubbed polyimide layer assembled for parallel alignment. Calibrated rodlike 5 μm polymer spacers controlled cell spacing.

Cells with the suspension or pure LC had identical alignment quality. Within experimental error, we measured the same value of the pretilt angle$=3.5°\pm 0.5°$ for both cells. Also, the clear points T_c of the suspensions and the LCs were essentially the same ($T_{c,\text{LC}}=92.3\,°C$, $T_{c,\text{susp}}=92.6\,°C$ for ZLI 4801; $T_{c,\text{LC}}=T_{c,\text{susp}}$ 35.4 for 5CB). Cells made with the particle suspension were stable for at least six months.

It is difficult to directly characterize the morphology of the suspended particles particularly dispersed in the anisotropic LC host. We used scanning electron microscopy (SEM) to image particles precipitated on a substrate from the matrix. The precipitated particles were $\leqslant 200$ nm in diameter and the distance between particles is more than 1 μm. The particles were clearly separated and did not form clusters. This large distance between particles and the stability of the suspension means interparticle interaction can be neglected.

We know that $Sn_2P_2S_6$ crystals are monoclinic before milling with a platelike shape. Our SEM analysis of the milled microparticles suggests they also have an anisotropic shape. Their orientation in the LC matrix will be determined by the orientational elastic energy of the LC, and by the anchoring energy of the LC at the particle surface. However, an anisotropic shape is not required to produce alignment of the particles. The permanent dipole moments of the particles will couple with the LC dielectric anisotropy and align with the director.

The LC matrix and the particles are both dielectrically

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[a] Author to whom correspondence should be addressed; electronic mail: johnwest@lci.kent.edu

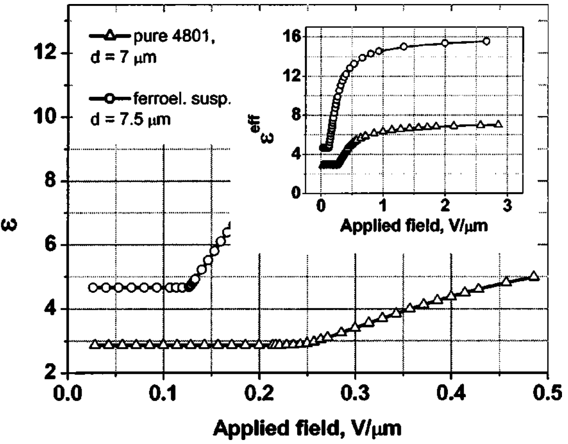

FIG. 1. The dependence of the effective dielectric constant ε^{eff} on the applied field.

anisotropic, both rotate in an applied electric field to minimize the total free energy. The resulting dielectric torques for the LC matrix and the particles are proportional to $\varepsilon_a^{\text{LC}}E_{\text{ac}}^2$ and $\varepsilon_a^{\text{particle}}E_{\text{ac}}^2$, respectively, where ε_a is the dielectric anisotropy. Since $\varepsilon_a^{\text{particles}} \gg \varepsilon_a^{\text{LC}}$, the particles give the main contribution to the torque even at their low concentration. Anchoring aligns the LC with the particles. The suspension can, therefore, be characterized by an effective dielectric anisotropy $\varepsilon_a^{\text{susp}}$ as if the particles acted as a molecular additive. As noted herein, we neglect interaction between the particles and, therefore, in the zero-order approximation, $\varepsilon_a^{\text{susp}}$ is equal:

$$\varepsilon_a^{\text{susp}} = (1 - f_\nu)\varepsilon_a^{\text{LC}} + f_\nu \varepsilon_a^{\text{particles}}, \tag{1}$$

where f_ν is the volume fraction of the particles. For reason values of $\varepsilon_a^{\text{particles}} \approx 10^3$ (Ref. 12) and $\varepsilon_a^{\text{LC}} = 3$ (Ref. 14), the suspension ($f_\nu = 0.003$) has a greatly enhanced dielectric anisotropy of $\varepsilon_a^{\text{susp}} \approx 6$.

We verified the increase in the dielectric anisotropy of the suspension by comparing the electro-optical response of the planar cell filled with the pure LC ZLI-4801 and the particle suspension. The dependence of the effective dielectric constant ε^{eff} of the LC on the applied field is shown in Fig. 1. Below the Freedericksz transition, V_{th}, the director aligns with the pretilt angle 3.5° on the surface and $\varepsilon^{\text{eff}} \approx \varepsilon_\perp$. At high enough voltages, the LC aligns with the field and $\varepsilon^{\text{eff}} \approx \varepsilon_{\text{II}}$. The threshold voltage of the Freedericksz transition for the suspension is $V_{\text{th}}^{\text{susp}} = 0.91$ V; just half that for the pure LC, $V_{\text{th}}^{\text{LC}} = 1.87$ V. This difference in the threshold can be estimated by the expression for the Freedericksz transition:[14]

$$V_{\text{th}} \propto \sqrt{K/\varepsilon_a}. \tag{2}$$

Because the tilt angle and elastic constants are the same for both cells, the difference in the threshold is totally the result of differences in the dielectric anisotropy and, therefore,

$$V_{\text{th}}^{\text{LC}}/V_{\text{th}}^{\text{susp}} \approx \sqrt{\varepsilon_a^{\text{susp}}/\varepsilon_a^{\text{LC}}} \tag{3}$$

From Fig. 1, one can see that $\varepsilon_{\text{II}}^{\text{LC}} \approx 7$, $\varepsilon_{\text{II}}^{\text{susp}} \approx 15.7$, $\varepsilon_\perp^{\text{LC}} \approx 3$, and $\varepsilon_\perp^{\text{susp}} \approx 4.6$. This means that $V_{\text{th}}^{\text{LC}}/V_{\text{th}}^{\text{susp}} \approx 1.7$, which is close to the experimental values $V_{\text{th}}^{\text{LC}}/V_{\text{th}}^{\text{susp}} = 1.9$. From the experimental data, $\varepsilon_\perp^{\text{susp}}$, and formula (1), one can estimate the value of dielectric anisotropy of the particles εaparticles ≈ 2400. This value is in the range of the report values of $\varepsilon_a^{\text{particles}}$ for $Sn_2P_2S_6$.[12]

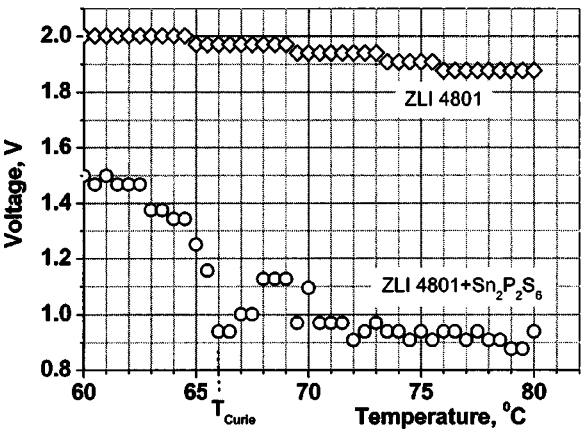

FIG. 2. The threshold voltage as a function of temperature for cells filled with the suspension and the pure LC.

The influence of the particles is clearly revealed by the change in the electro-optic response with temperature. As expected, the pure LC threshold voltage gradually decreases with temperature because of the weak temperature dependence of $K/\varepsilon_{\text{LC}}(T)$. The threshold for the suspension also decreases with temperature because of the weak temperature dependence of $K/\varepsilon_{\text{LC}}(T)$. However, the unique dielectric properties of the ferroelectric suspensions become apparent at the Curie temperature of the $Sn_2P_2S_6$ where the threshold voltage for the suspension changes abruptly (Fig. 2). This is the result of the critical behavior of the dielectric anisotropy at this temperature.[15,16] While we do not understand all the details of this abrupt change, we can obtain an experimental value of the Curie temperature from Fig. 2 of 66 °C, exactly the same as determined for the bulk $Sn_2P_2S_6$ crystals.

The permanent dipoles in the LC/particle suspension are randomly aligned in a head-to-tail fashion [Fig. 3(a)]. Therefore, in order to realize the ferroelectric properties of the particles, we applied a large dc-electric field, sufficient to break the symmetry and align the particle dipoles along the field [Fig. 3(b)]. A low-frequency ac field applied perpendicular to the dc field rotates the particles to the right-or

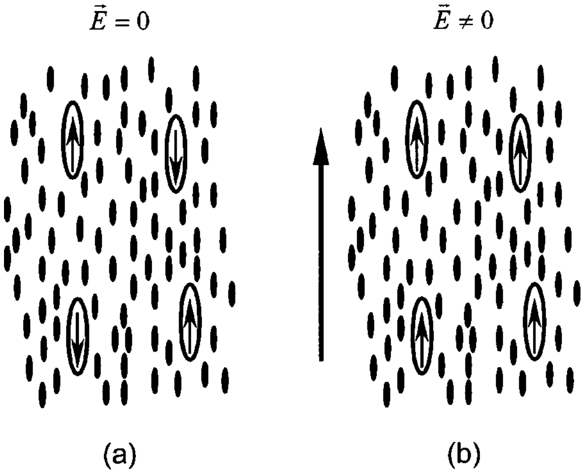

FIG. 3. Schematic representation of the ferroelectric particles in an LC. (a) The permanent dipoles of the particles are equally distributed in the plus and minus directions. (b) dc-electric field aligns the particle dipoles along the field, breaking the plus–minus symmetry.

left-hand side depending on the sign of the applied field. The resulting linear component of the electro-optic response of the suspension will be proportional to both the polarizing dc and the deflecting ac fields.

To prove the unusual linear response of a nematic to *an electric* vector **E**, we carried out the experiment inspired by the work of Kang and Rosenblatt[17] on the surface-induced linear electro-optic effect in nematic LC. We studied the electro-optic response of an LC cell composed of one substrate with a continuous ITO conducting surface and one with interdigitated ITO electrodes with a mm distance between lines allowing the application of an in-plane field. Both substrates were identically treated for homeotropic alignment of 5CB. An ac field $E_{\mathrm{ac}}(0-100\ \mathrm{V},\ 1\ \mathrm{kHz})$ was applied in the plane of the cell and the dc field $E_{\mathrm{dc}}(0-30\ \mathrm{V})$ was applied perpendicular to the plane of the cell (along the director of the suspension). The voltage of the ac fields was below the voltage of the Freedericksz transition.

Light from a He–Ne laser passed through a polarizer, the cell, a crossed analyzer, and then into a photodiode detector. The beam was narrow enough to pass through the 1 mm interelectrode gap in the cell. The cell was tilted at 45° with respect to the beam and the interdigitated electrodes are aligned 45° to the beam polarization direction. The detector output, proportional to the total light intensity *I*, was fed into a lock-in amplifier referenced to the ac driving voltage $U_{\mathrm{ac}}(\omega)$. The key to this experiment is the 45° of the cell relative to the beam, producing a different optical retardation for the right-or left-hand side rotation of the suspension resulting from opposite signs of the ac field.

The dependence of the linear component of the electro-optic response of the suspension and the pure LC as a function of the applied ac voltage $(\nu = 200\ \mathrm{Hz})$ (Ref. 18) for different values of the polarizing dc field is shown in Fig. 4. As expected, the pure LC responds only to the magnitude and not the sign of the field for the whole dc field range and, therefore, shows no response in our experimental setup. There was also no linear response of the suspension when no dc field was applied. Application of the dc field resulted in the appearance of the sign-sensitive component of the electro-optical response, which increased proportionally to both the magnitude of the dc and the ac fields. Switching off of the dc field resulted in the fast disappearance of the linear response $(\tau_{\mathrm{decay}} \leqslant 2\ \mathrm{ms})$, and is caused by the disordering of the ferroelectric particles by thermal fluctuation. The characteristic time of rotation of a rodlike particle in a liquid with viscosity γ can be estimated by the formula $\tau_{\mathrm{decay}} = \gamma L^3/k_B T$,[19] which gives for reasonable values of $\gamma = 0.1\ \mathrm{P}$, $L = 100\ \mathrm{nm}$ and $T = 300\ \mathrm{K}$ a value of $\tau_{\mathrm{decay}} \approx 2.5\ \mathrm{ms}$.

In conclusion, we observed that dispersing low concentrations of submicron ferroelectric particles in a nematic LC enhances the dielectric response and induces a linear response to the electric vector **E** in a nematic. In contrast to molecular additives, these particle dispersions substantially lower the operating voltage of LC displays and related devices.

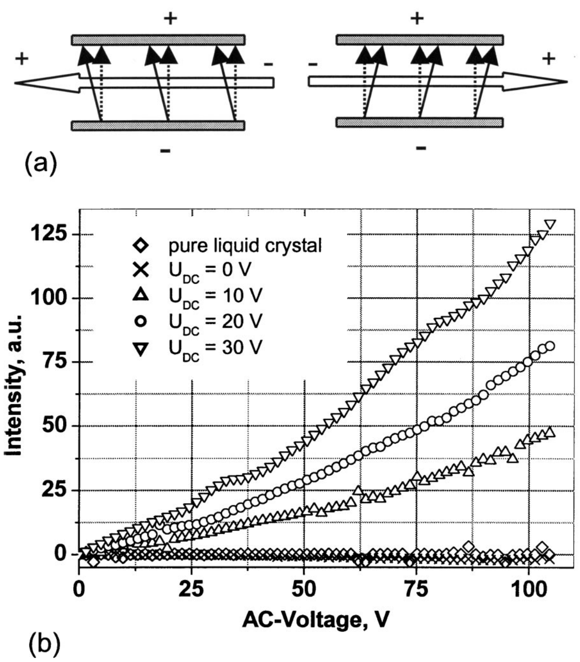

FIG. 4. Linear response of the suspension upon application of an ac-electric field. (a) The substrate with striped electrodes with an ac field in the plane of the cell and a dc field applied perpendicular to the plane of the cell (along the director of the suspension). (b) The dependence of the linear component of the electro-optic response of the suspension and the pure LC as a function of the applied ac voltage for different values of the polarizing dc field.

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