Ferro-nematics and their outlook

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Abstract. We report on the development of ferronematic liquid crystals, new materials that consist of a dilute suspension of ferroelectric particles in a nematic liquid crystal host. The particles share their ferroelectric properties with the nematic liquid crystal and impose a spontaneous dielectric polarization of about 10 nC/cm^2 to the entire medium, typical for many ferroelectric liquid crystals. As expected, these new materials have enhanced dielectric anisotropy and are sensitive to the sign of an applied electric field. The potential of their use in a number of devices are discussed.

Introduction. Long-range forces between ultra-fine particles imbedded in liquid crystal matrices produce intriguing colloids [1-4]. For example, dispersed ferromagnetic particles greatly enhance the magnetic properties of the liquid crystal [1]. Large (>>μm) colloidal particles form defects in liquid crystal matrices producing large director deformations. Ensembles of these particles and defects can form complex structures [2]. High concentrations (> 2-3% by weight) of sub-micron particles can create almost rigid liquid crystal suspensions [3-4].

Here we show that at low concentrations, liquid crystal colloids behave as a pure liquid crystal with no evidence of dissolved particles, but have enhanced properties. These dilute suspensions are stable, because the nano-particles do not significantly perturb the director field in the liquid crystal, and interaction between the particles is weak. Importantly, the nanoparticles share their intrinsic properties with the liquid crystal matrix due to the alignment with the liquid crystal. In particular, doping a nematic liquid crystal matrix with ferro-electric nanoparticles produces enhanced dielectric anisotropy and introduces the ferro-electric properties inherent to the nanoparticles.

Experiments and results. We used particles of the ferro-electric thiohypodiphosphate ($Sn_2P_2S_6$) for the suspension. At room temperature $Sn_2P_2S_6$ has a spontaneous polarization of 14 μC cm^{-2} parallel to the [101] direction of the monoclinic cell [5]. 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 [6].

We obtained small ferro-electric particles by milling large particles (≅1 μm size) as opposed to chemical fabrication because milling can be used to produce smaller (10 nm) ferro-electric particles. The particles were ultrasonically dispersed and ground in a vibration mill. The resulting ferro-electric particles were mixed with a solution of oleic acid (surfactant) in heptane. The resulting ferro-electric particle suspension was mixed with the liquid crystal. The heptane was then evaporated and the mixture was ultrasonically dispersed. The relative concentrations of components were adjusted to give a final suspension with about 0.3 % by volume of ferro-particles.

Planar cells were filled with the liquid crystal suspension or pure liquid. The cells consisted of two ITO coated glass substrates with a rubbed polyimide layer assembled for parallel alignment. Calibrated rod-like, 5 μm polymer spacers controlled cell spacing.

It is difficult to directly characterize the morphology of the suspended particles when dispersed in the anisotropic liquid crystal host. We used scanning electron microscopy to image particles precipitated on a substrate from the matrix. The precipitated particles were ≤ 200 nm in diameter and the distance between particles is more than 1 μm. The particles were clearly separated and did not form clusters. The large distance between particles and the stability of the suspension means inter-particle interaction can be neglected.

We know that $Sn_2P_2S_6$ crystals are monoclinic before milling with a plate-like shape. Our SEM analysis of the milled microparticles suggests they also have an anisotropic shape. Their orientation in the liquid crystal matrix will be determined by the orientational elastic energy of the liquid crystal, and by the anchoring energy of the liquid crystal 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 liquid crystal dielectric anisotropy and align with the director.

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 liquid crystal ZLI-4801 and the particle suspension. Below the Freedericksz transition, V_{th}, the director aligns with the pretilt angle of 3.5° on the surface and $\varepsilon^{eff} \approx \varepsilon_{\perp}$. At high enough voltages the liquid crystal aligns with the field and $\varepsilon^{eff} \approx \varepsilon_{II}$. The threshold voltage of the Freedericksz transition for the suspension is $V_{th}^{susp} = 0.91\text{V}$ just half that for the pure liquid crystal, $V_{th}^{LC} = 1.87\text{V}$.

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

The permanent dipoles in the liquid crystal /particle suspension are randomly aligned in a head to tail fashion. Therefore, in order to realize the ferro-electric properties of the particles we applied a large *dc*-electric field, sufficient to break the symmetry and align the particle dipoles along the field. A low frequency *ac*-field applied perpendicular to the *dc* field rotates the particles right or left depending on the sign of the applied field. The resulting linear component of the electro-optic response of the suspension is proportional to both the polarizing, *dc*-, and the deflecting *ac*-fields.

As expected the pure liquid crystal 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 set-up. 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*-field. Switching off of the *dc*-field resulted in the fast disappearance of the linear response ($\tau_{decay} \leq$ 2 ms), and is caused by the disordering of the ferro-electric particles by thermal fluctuation. The characteristic time of rotation of a rod-like particle in a liquid with viscosity γ can be estimated by the formula $\tau_{decay} = \gamma L^3 / k_B T$ [Ref 19], which gives for reasonable values of γ = 0.1P, L = 100nm and T = 300K a value of $\tau_{decay} \approx 2.5\text{ms}$.

Conclusions. We observed that dispersing low concentrations of sub-micron ferro-electric particles in a nematic liquid crystal enhances the dielectric response and induces a linear response to the electric vector $\vec{E}$ in a nematic. In contrast to molecular additives these particle dispersions substantially lower the operating voltage of liquid crystal displays and related devices.

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