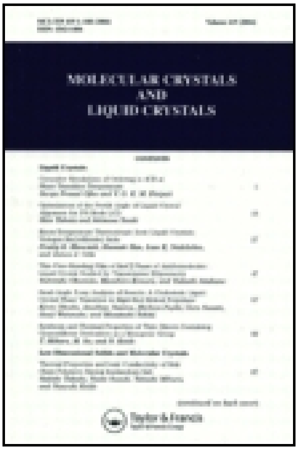

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EFFECTIVE DIELECTRIC FUNCTION OF FERROELECTRIC LC SUSPENSIONS

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We study dielectric properties of a dilute suspension of ferroelectric particles in a nematic liquid crystal (LC) host. It is supposed that submicron particles do not disturb the LC alignment and the suspension macroscopically appears similar to a pure LC. We propose theoretical model for effective dielectric function of ferroelectric LC suspension. It is found that particles permanent polarisation may significantly increase the effective value of suspension dielectric function in comparison with pure LC. For more elongated particles depolarisation factor is smaller and respectively the contribution of induced polarisation of particles to the effective dielectric function is higher.

Keywords: anchoring; liquid crystals; memory effect

INTRODUCTION

It is known that sensitivity of isotropic liquid to the electric field can be gained by doping with ultra-fine (less then 1 μm size) ferro-electric particles [1–4]. Bachmann and Barner showed that a long milling process of ferro-electric $BaTiO_3$ particles in the presence of surfactant can result in a stable suspension of ultra-fine particles of $BaTiO_3$ in heptane. It was shown that the particles have an average radius of about 10 nm. They are ferro-electric single crystals and carry a permanent dipole moment about 2000 Debye. It allows effectively control a birefringence in the suspension by application of electric field that is impossible in a heptane matrix itself. Recently we reported on the successful development of a dilute suspension of ferroelectric particles in a nematic liquid crystal (LC) host [5,6]. We found that the submicron particles of $Sn_2P_2S_6$ do not disturb the LC

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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. The value of the parallel component of the suspension dielectric function was almost two times higher that one of pure LC.

MODEL AND CALCULATIONS

To get simplified qualitative effect of ferroelectric particles onto sample polarization under the external electric field (and therefore particles influence on the effective dielectric function) we shall suppose the following:

- ferroelectric articles are spheroids with long axis oriented along local LC director **n**, particle's volume is v;
- orientation of main axis of particles polarizability tensor coincides with particles long axis and local LC director, main values of particles dielectric function are $\varepsilon_{||}^{P}$(along particles long axis) and $\varepsilon_{\perp}^{P}$ (in plane perpendicular to long axis);
- each particle possesses *permanent polarization* **d**, which is supposed to be *parallel* or *anti-parallel* to the local LC director **n**;
- in the absence of externally applied electric field both directions of permanent polarization have equal probability, and averaged over physically small volume permanent polarization is zero.

The *induced polarization* of particles has the form

$$p_i = \varepsilon_0\left((\varepsilon_{\perp}^{P} - 1)E_i^P + \varepsilon_a^P n_i n_j E_j^P\right). \tag{1}$$

here $\varepsilon_a^P = \varepsilon_{||}^P - \varepsilon_{\perp}^P$ is the anisotropy of ferroelectric particles dielectric function, $\mathbf{E}^{\mathrm{P}}$ is the local electric field that acts onto particle. The averaged value of particle *permanent* polarization in LC matrix, $\tilde{\mathbf{d}}$, depends on frequency and magnitude of the applied electric field. It may be written as

$$\tilde{\mathbf{d}} = \langle \mathbf{d}(\mathbf{E}) \rangle_{LC} = \int \mathbf{d} f(\mathbf{d}, \mathbf{n}, \mathbf{E})\, d\Omega \tag{2}$$

here $f(\mathbf{d}, \mathbf{n}, \mathbf{E})$ is the permanent polarization distribution function and **E** is the electric field that orients permanent polarization. This field differs from $\mathbf{E}^{\mathrm{P}}$, it does not include field of permanent polarisation inside particle.

In the simplest form for low frequency electric field we may model orientation of permanent particles polarization as two level system and get respectively

$$\langle \mathbf{d}(\mathbf{E})\rangle_{LC} = d\mathbf{n}\frac{\exp\left(d\frac{\mathbf{nE}}{k_BT}v\right) - \exp\left(-d\frac{\mathbf{nE}}{k_BT}v\right)}{\exp\left(d\frac{\mathbf{nE}}{k_BT}v\right) + \exp\left(-d\frac{\mathbf{nE}}{k_BT}v\right)}$$

At low electric field in the above mentioned two-level model we get

$$\langle \mathbf{d}(\mathbf{E})\rangle_{LC} = d^2 v\mathbf{n}\frac{\mathbf{nE}}{k_BT},$$

here the magnitude of permanent polarization depends on temperature, $d(T)$, this dependence may be especially strong nearby the Curie temperature. In the isotropic phase permanent polarization input is either zero (if we are above the Curie point) or is about three times less. This is because in the isotropic phase we don't have any more two level model and averaging over all possible orientation of particles gives

$$\langle \mathbf{d}(\mathbf{E})\rangle_{I} = d^2 v\mathbf{n}\frac{\mathbf{nE}}{3k_BT}$$

Both *induced* polarization and *averaged permanent* polarization give rise to the total polarization of particle $\mathbf{P} = \mathbf{p} + \tilde{\mathbf{d}}$. Input of particles to the total polarisation of suspension is proportional to their concentration.

Now to introduce effective dielectric function of the suspension we average the electric field over physically small volume thought still containing large enough amount of particles

$$\overline{\mathbf{E}} = f\left\langle \mathbf{E}^P\right\rangle + (1-f)\left\langle \mathbf{E}^{LC}\right\rangle \tag{3}$$

where $\left\langle \mathbf{E}^P\right\rangle$ and $\left\langle \mathbf{E}^{LC}\right\rangle$ are averaged over physically small volume values of electric field inside particles and LC. Similarly for the dielectric displacement

$$\begin{aligned}\overline{\mathbf{D}} &= f\left\langle \mathbf{D}^P\right\rangle + (1-f)\left\langle \mathbf{D}^{LC}\right\rangle \\ &= f\left\langle \varepsilon_0\mathbf{E^P} + \tilde{\mathbf{d}} + \varepsilon_0\left(\varepsilon^P - I\right)\mathbf{E^P}\right\rangle + (1-f)\left\langle \varepsilon_0\mathbf{E^{LC}} + \varepsilon_0\left(\varepsilon^{LC} - I\right)\mathbf{E^{LC}}\right\rangle\end{aligned} \tag{4}$$

or in the direction parallel to the LC director and in the plane perpendicular to it

$$\begin{aligned}\overline{D}_{||} &= f\left(\varepsilon_0\left\langle E^P_{||}\right\rangle + \frac{d^2}{k_BT}v\left\langle \left(E^P_{||} - E_d\right)\right\rangle + \varepsilon_0\left(\varepsilon^P_{||} - 1\right)\left\langle E^P_{||}\right\rangle\right) \\ &\quad + (1-f)\left(\varepsilon_0\left\langle E^{LC}_{||}\right\rangle + \varepsilon_0\left(\varepsilon^{LC}_{||} - I\right)\left\langle E^{LC}_{||}\right\rangle\right) \\ \overline{D}_{\perp} &= f\left(\varepsilon_0\left\langle E^P_{\perp}\right\rangle + \varepsilon_0\left(\varepsilon^P_{\perp} - 1\right)\left\langle E^P_{|\perp}\right\rangle\right) \\ &\quad + (1-f)\left(\varepsilon_0\left\langle E^{LC}_{\perp}\right\rangle + \varepsilon_0\left(\varepsilon^{LC}_{\perp} - I\right)\left\langle E^{LC}_{\perp}\right\rangle\right)\end{aligned} \tag{5}$$

here E_d is the electric field of permanent polarisation inside particle.

We introduce mean dielectric function $\hat{\varepsilon}$ of our heterogeneous medium by relation

$$\overline{\mathbf{D}} = \hat{\varepsilon}\overline{\mathbf{E}} \tag{6}$$

To relate $\langle \mathbf{E}^P \rangle$ and $\langle \mathbf{E}^{LC} \rangle$ with $\overline{\mathbf{E}}$ one needs the dependence between $\langle \mathbf{E}^P \rangle$ and $\langle \mathbf{E}^{LC} \rangle$. We shall suppose that this dependence is linear

$$\langle \mathbf{E}^P \rangle = \hat{T} \langle \mathbf{E}^{LC} \rangle \tag{7}$$

and matrix $\hat{T}$ is the same as for single spheroid with permanent polarisation $\tilde{\mathbf{d}}$ and isotropic dielectric function $\tilde{\varepsilon}^P = \frac{1}{3} Sp\varepsilon^P$ placed in the isotropic host with dielectric function $\tilde{\varepsilon}^{LC} = \frac{1}{3} Sp\varepsilon^{LC}$ (similar assumptions were employed by Maier and Meier to derive the dielectric function of pure LC).

Now we consider a single isotropic spheroid with permanent polarisation $\tilde{\mathbf{d}}$ immersed in the isotropic host. A voltage is applied between the condenser plates such that the volume averaged field in the system is $\mathbf{E}_0^{\mathbf{LC}}$. The electric field $\mathbf{E}^{\mathbf{P}}$and the displacement field $\mathbf{D}^{\mathbf{P}}$ inside the inclusion are uniform and satisfy the exact relation [7]

$$(1-\lambda_i)\varepsilon_0 \tilde{\varepsilon}^{LC} E_i^P + \lambda_i D_i^P = \varepsilon_0 \tilde{\varepsilon}^{LC} E_{0,i}^{LC} \tag{8}$$

where $\lambda_{||} = \frac{1-e^2}{e^3}(\text{arth} e - e)$, $\lambda_\perp = \frac{1}{2}\left(1-\lambda_{||}\right)$ are the depolarization factors, $e = \sqrt{1-b^2/a^2}$ is the spheroid's eccentricity, and $a, b(a > b))$ are the semi-axes of spheroid.

From this formula it is easy to find

$$E_\perp^P = \frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_\perp(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})} E_{0,\perp}^{LC}$$

$$E_{||}^P = \frac{\tilde{\varepsilon}^{LC} E_{0,||}^{LC} - \lambda_{||}\frac{\tilde{d}}{\varepsilon_0}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})}$$

It is seen now that electric field determining averaged value $\tilde{d}$ is given by

$$\tilde{E}_{||}^P = \frac{\tilde{\varepsilon}^{LC} E_{0,||}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})},$$

therefore

$$\tilde{d} = \frac{d^2 v}{k_B T} \frac{\tilde{\varepsilon}^{LC} E_{0,||}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})}$$

and

$$E_{||}^P = \frac{\tilde{\varepsilon}^{LC} - \lambda_{||}\frac{d^2 v}{\varepsilon_0 k_B T}\frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})}}{\tilde{\varepsilon}^{LC} + \lambda_{||}(\tilde{\varepsilon}^P - \tilde{\varepsilon}^{LC})} E_{0,||}^{LC}$$

Finally, we get

$$\hat{T} = \begin{pmatrix} \frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{\perp}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})} & 0 & 0 \\ 0 & \frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{\perp}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})} & 0 \\ 0 & 0 & \frac{\tilde{\varepsilon}^{LC}-\frac{\lambda_{||}d^2v}{\varepsilon_0 k_B T}\frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})}}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})} \end{pmatrix} \quad (9)$$

From Eq. (7) we also find that permanent polarisation of spheroid particles creates the following electric field inside the particle:

$$E_d = -\frac{\lambda_{||}}{\varepsilon_0}\frac{1}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})}\frac{d^2v}{k_B T}\frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})}E_{0,||}^{LC} \quad (10)$$

Substituting (3), (7), (9) into (5) we find effective dielectric function of the suspension

$$\tilde{\varepsilon}_{\perp} = \frac{fT_{\perp}\varepsilon_{\perp}^{P} + (1-f)\varepsilon_{\perp}^{LC}}{1-f+fT_{\perp}} \quad (11)$$

$$\tilde{\varepsilon}_{||} = \frac{fT_{||}\varepsilon_{||}^{P} + (1-f)\varepsilon_{||}^{LC} + f\frac{d^2v}{\varepsilon_0 k_B T}\frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})}}{1-f+fT_{||}} \quad (12)$$

Note that formulae (11) does not contain permanent polarisation of ferroelectric particle and it is exactly the same as Maxwell-Garnett [8] expression for effective dielectric function. To get some contribution from permanent polarisation to $\tilde{\varepsilon}_{\perp}$ one has to assume non-zero angle between particles permanent polarisation and long axis, or allow particles to be not perfectly aligned with respect to director.

It is also seen that for small concentration of particles, $f \ll 1$, $\tilde{\varepsilon}_{\perp} \approx fT_{\perp}\varepsilon_{\perp}^{P} + (1-f)\varepsilon_{\perp}^{LC}$ and even if we take particles with $\varepsilon_{\perp}^{P} \gg \varepsilon_{\perp}^{LC}$ the effective dielectric function component $\tilde{\varepsilon}_{\perp}$ will not much differ from $\varepsilon_{\perp}^{LC}$ because $T_{\perp} \sim \frac{\tilde{\varepsilon}^{LC}}{\lambda_{\perp}\tilde{\varepsilon}^{P}}$

Situation is different for parallel component of the effective dielectric function. Here the additional contribution due to permanent polarisation is

$$\delta\tilde{\varepsilon}_{||} = f\frac{d^2v}{\varepsilon_0 k_B T}\frac{\tilde{\varepsilon}^{LC}}{\tilde{\varepsilon}^{LC}+\lambda_{||}(\tilde{\varepsilon}^{P}-\tilde{\varepsilon}^{LC})}$$

This term at high enough values of permanent polarisation may significantly increase the effective value of $\tilde{\varepsilon}_{||}$. It should be also noted that more elongated the particle the smaller depolarisation factor $\lambda_{||}$, and respectively even in the absence of permanent polarisation the parallel component of the effective dielectric function gets higher gain in comparison with the perpendicular component. For instance, if the aspect ratio $b/a = 0.1$, then $\lambda_{||} \approx 0.02$, $\lambda_{\perp} \approx 0.49$, and for $\varepsilon^{P}_{\perp,||} \gg \varepsilon^{LC}_{\perp,||}$ we have $\frac{\delta\tilde{\varepsilon}_{||}(d=0)}{\delta\tilde{\varepsilon}_{\perp}} \sim \frac{\lambda_{\perp}\varepsilon^{P}_{||}}{\lambda_{||}\varepsilon^{P}_{\perp}} \gg 1$.

ESTIMATES AND CONCLUSION

To get numerical estimation of possible increase of the effective dielectric function of ferroelectric suspension due to particles permanent polarisation we assume the following numbers. The characteristic dimensions of the particles in the suspension are 100 nm*30 nm*30 nm and their volume fraction is 10^{-4} in the LC matrix. Spontaneous polarization of $Sn_2P_2S_6$ particles is 10 μC/cm^2 [9]. Dielectric constant $\tilde{\varepsilon}^{LC} \approx 4$. The value of dielectric constant of $Sn_2P_2S_6$ along the main axis strongly depends on the quality of the samples and varies from 200 for ceramics sample to 9000 for monodomain crystals [10], so we shall use 3000 for $\tilde{\varepsilon}^{P}$. Now we obtain $\delta\tilde{\varepsilon}_{||} \approx 10$ that is very close to the experimental data [6].

To develop more sophisticated theory and describe the experimental data more accurately one has to use in (2) the orientational distribution function for particles different from that given by two-level system, take account of LC host and particles dielectric anisotropy (it will change the exact form of matrix T in expression (9)), assume non-zero angle between permanent polarisation and particle long axis.

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