Open access • Journal Article • DOI:10.1080/15421400600654108

Fredericksz Transition Threshold in Nematic Liquid Crystals Filled with Ferroelectric Nano-Particles — Source link

V. Yu. Reshetnyak, Sergii M. Shelestiuk, Timothy J. Sluckin

Institutions: Taras Shevchenko National University of Kyiv, University of Southampton

Published on: 22 Sep 2006 - Molecular Crystals and Liquid Crystals (Taylor & Francis Group)

Topics: Liquid crystal, Polarization density and Ferroelectricity

Freedericksz transition threshold in nematic liquid crystals filled with ferroelectric nanoparticles

V.Yu. Reshetnyak[a], S.M. Shelestiuk[a] and T.J. Sluckin[b]

[a]Physics Faculty, Kyiv National Taras Shevchenko University

Prospekt Glushkova, 03680 Kyiv, Ukraine

phone : +38044 5264477, fax +38044 5250830,

e-mails: reshet@iop.kiev.ua, sergi@ua.fm

[b]School of Mathematics, University of Southampton,

Southampton SO17 1BJ, UK

phone: +4423 8059 3680, fax: +4423 8059 5147,

e-mail: T.J.Sluckin@soton.ac.uk

Abstract

A key liquid crystalline property for electro-optic applications is the Frederiks threshold electric field. There has been recent experimental interest in liquid crystal-based colloidal suspensions in which the colloidal nanoparticles both possess a permanent electric polarization and provide strong director anchoring on the particle surface. Such suspensions are sometimes known as Filled Liquid Crystals. Our calculations suggest, in qualitative agreement with experiment, that filling the nematic liquid crystal with ferroelectric nanoparticles can significantly decrease the electric Frederiks transition threshold field.

Keywords: liquid crystal suspensions, Frederiks transition, ferroelectric particles

1. INTRODUCTION

In recent years there has been much interest in the physics and possible technological applications of colloidal suspensions in a liquid crystal host [1]. As early as 1970, Brochard and de Gennes [2] pointed out that if the colloidal particles possess a permanent magnetic moment, then the orientation of the local moments and the nematic director would be coupled, and this would give rise to some new and interesting physical effects. These systems are known as ferronematics, and further work, both experimental and theoretical, seems to confirm the picture predicted by Brochard and de Gennes [3-5].

A system analogous to this, but in which potentially much more dramatic effects might be expected, involves ferroelectric rather than ferromagnetic colloidal particles. Such systems have been fabricated by Reznikov *et al* [6], who have shown that at low concentrations, at least in some cases, these submicron colloids appear similar to a pure liquid crystal. In particular, the colloidal particles do not scatter light in the manner that we might expect, and are therefore invisible. The particles are engineered so as to anchor the liquid crystal director strongly at the surface. It is this mechanism which seems to permit the intrinsic properties of the colloidal particles to influence the liquid crystal matrix. A further unexpected observation is that in these suspensions the Frederiks transition threshold voltage decreases. If this phenomenon could be replicated, there would be significant implications for the manufacture of very low power liquid crystal displays.

In this brief report we present a very simple theoretical model for electric Frederiks transition threshold in the ferroelectric liquid crystal suspension. The theory uses the following minimal postulates: *(a)* the colloidal particles do not affect the elastic and dielectric properties of liquid crystalline host; *(b)* each particle possesses a permanent polarization which can only be parallel or antiparallel to the local LC director; *(c)* there is no direct inter-particle interaction; *(d)* the field-induced polarization of the colloidal particles can be neglected. Condition (b) is sometimes known as *strong director anchoring* in related contexts. Hypotheses *(a-d)* can be relaxed in principle, and should be relaxed in a complete theory. Nevertheless they contain sufficient physics that they may be regarded as a sensible starting point. Our simple theory predicts that filling the nematic liquid crystal with ferroelectric nanoparticles may significantly decrease the electric Fredericks transition threshold voltage.

2. BASIC EQUATIONS

We consider a uniform colloidal suspension of ferroelectric submicron particles embedded in a liquid crystalline host. The liquid crystal is placed in a cell of thickness L with identical homogeneous (i.e. planar and uniform) boundary conditions at each wall. A voltage V is applied across the cell. We assume the coupling between the permanent polarization of the colloidal particle and the liquid crystalline director to be sufficiently strong that the particle orientation is restricted to directions parallel or antiparallel to the local director. The theory is an extension of the basic ideas used by de Gennes and coworkers [2], and is related to an analogous theory for ferronematics [5], with an additional complication of local field effects.

A free energy functional for the suspension is minimized with respect to relevant variables. The functional includes elastic, electric and entropy terms and takes the form:

$$F = F_{el} + F_E + F_{entr}, \tag{1}$$

where

$$F_{el} = \frac{1}{2}\int_0^L \left(K_1(\operatorname{div}\vec{n})^2 + K_2(\vec{n}\cdot\operatorname{curl}\vec{n})^2 + K_3[\vec{n}\times\operatorname{curl}\vec{n}]^2\right)dz,$$

$$F_E = -\frac{1}{2}\int_0^L \vec{D}_0\cdot\vec{E}\,dz - \int_0^L \vec{P}\cdot\vec{E}_0\,dz,$$

$$F_{entr} = \int_0^L f\frac{kT}{v}\left(\rho_+\ln\rho_+ + \rho_-\ln\rho_-\right)dz.$$

The meaning of the quantities in eq.(1) is as follows

Definition	Description
$\vec{D}_0 = \varepsilon_0 \hat{\varepsilon} \vec{E}$	Electric displacement due to liquid crystalline effects alone.
$\vec{D} = \vec{D}_0 + \vec{P}$	Total electric displacement, including both colloidal and liquid crystalline effects
$\vec{E}_0 = \lambda \vec{E}$	Local electric field felt by a colloidal particle, and which enters particle permanent polarization expression
λ	Local field correction factor
$\vec{P} = fd\vec{n}(\rho_+ - \rho_-)$	Permanent polarization per unit volume in the colloid
d	Permanent polarization of a particle
f	Particle volume fraction in the suspension
ρ_+, ρ_-	Fractions of ferroelectric particles oriented parallel and antiparallel to the local LC director respectively
v	Particle volume
K_i	Frank-Oseen elastic constants of liquid crystal

Table 1: Meanings of quantities used in this paper.

The problem here is to minimize the functional (1) subject to the constraint of given voltage V applied across the cells:

$$V = \int_0^L E_z(z)dz \tag{2}$$

Supposing the nematic to be an ideal dielectric, we write $\operatorname{div}\vec{D} = 0$ or $\frac{\partial D_z}{\partial z} = 0$ (there is no dependence on x and y coordinates.) Solving this, we obtain $D = D_z = const$. Likewise, combining the conditions $\operatorname{curl}\vec{E} = 0$ the boundary conditions $E_x = E_y = 0$ at the cell walls, yields the intuitively obvious $\vec{E} = (0, 0, E(z))$.

Minimizing functional (1) with respect to $\rho_\pm$ subject to the constraint $\rho_+ + \rho_- = 1$ yields:

$$\rho_{\pm}=\frac{\exp\left(\pm\lambda dv\beta\left(\vec{E}\cdot\vec{n}\right)\right)}{\exp\left(\lambda dv\beta\left(\vec{E}\cdot\vec{n}\right)\right)+\exp\left(-\lambda dv\beta\left(\vec{E}\cdot\vec{n}\right)\right)}, \tag{3}$$

here $\beta=\frac{1}{kT}$.

Now we consider the splay Frederiks transition in the electric field. In this case the director field is given by $\vec{n}=\left(\cos\theta,0,\sin\theta\right)$. From Table 1, the dielectric displacement can be written as:

$$D=\varepsilon_0\left(\varepsilon_{\perp}+\varepsilon_a\sin^2\theta\right)E_z\left(\theta\right)+fd\left(\rho_{+}-\rho_{-}\right)\sin\theta \tag{4}$$

Combining expressions (3) and the free energy functional (1) gives the following explicit expression for the free energy functional (1), as a functional of the local director $\theta(z)$ and the local electric field $E_z(z)$:

$$F=\int_0^L\left\{\begin{array}{l}\frac{1}{2}\left(K_1\cos^2\theta+K_3\sin^2\theta\right)\theta'^2-\frac{1}{2}\varepsilon_0\left(\varepsilon_{\perp}+\varepsilon_a\sin^2\theta\right)E_z^2\left(\theta\right)-\\-\frac{f}{\beta v}\ln\left[\exp\left(\lambda dv\beta E_z\left(\theta\right)\sin\theta\right)+\exp\left(-\lambda dv\beta E_z\left(\theta\right)\sin\theta\right)\right]\end{array}\right\}dz, \tag{5}$$

where eq.(2) connects the field $E_z(z)$ to the voltage constraint.

In what follows we assume that ferroelectric particles are small enough, so that $\lambda dv\beta E<<1$. Then the total free energy functional (5) to be minimized becomes

$$F=\int_0^L\left\{\frac{1}{2}\left(K_1\cos^2\theta+K_3\sin^2\theta\right)\theta'^2-\frac{1}{2}\varepsilon_0\left(\varepsilon_{\perp}+\tilde{\varepsilon}_a\sin^2\theta\right)E_z^2\left(\theta\right)\right\}dz+const, \tag{6}$$

where $\tilde{\varepsilon}_a=\varepsilon_a+\frac{\lambda\left(\lambda+1\right)fd^2v\beta}{\varepsilon_0}$ is the effective dielectric function anisotropy.

Using eq. (4) we rewrite the constraint (2) in the form

$$V=\int_0^L\frac{D}{\varepsilon_0\left(\varepsilon_{\perp}+\varepsilon_a\sin^2\theta\right)+\lambda fd^2v\beta\sin^2\theta}dz. \tag{7}$$

For small angles θ we have:

$$E_z(\theta) \approx \frac{D}{\varepsilon_0\varepsilon_\perp}\left[1-\left(\frac{\varepsilon_a}{\varepsilon_\perp}+\frac{\lambda f d^2 v\beta}{\varepsilon_0\varepsilon_\perp}\right)\theta^2\right]. \tag{8}$$

The free energy functional simplifies to:

$$F=\int_0^L\left\{\frac{K_1}{2}\theta'^2-\frac{1}{2}\frac{D^2}{\varepsilon_0\varepsilon_\perp}\left[1-\left(\frac{\varepsilon_a}{\varepsilon_\perp}-\frac{\lambda(\lambda-1)fd^2v\beta}{\varepsilon_0\varepsilon_\perp}\right)\theta^2\right]\right\}dz+const, \tag{9}$$

subject to the constraint:

$$V=\int_0^L\frac{D}{\varepsilon_0\varepsilon_\perp}\left[1-\left(\frac{\varepsilon_a}{\varepsilon_\perp}+\frac{\lambda fd^2v\beta}{\varepsilon_0\varepsilon_\perp}\right)\theta^2\right]dz. \tag{10}$$

Trivially, eq. (10) also gives an expression for the displacement field as a function of V and the director profile:

$$D=\frac{\varepsilon_0\varepsilon_\perp V}{L}\left[1+\frac{1}{L}\left(\frac{\varepsilon_a}{\varepsilon_\perp}+\frac{\lambda fd^2v\beta}{\varepsilon_0\varepsilon_\perp}\right)\int_0^L\theta^2dz\right] \tag{11}$$

We now substitute D into the free energy functional (9) and minimize the total free energy functional with respect to the angle θ. The corresponding first integral of Euler-Lagrange equation has the form:

$$K_1\theta'^2+\left(\frac{V}{L}\right)^2\varepsilon_0\tilde{\varepsilon}_a\theta^2=const; \tag{12}$$

the additional conditions on the mid-plane of the cell, $\theta\left(\frac{L}{2}\right)=\theta_{\max}$ and $\theta'\left(\frac{L}{2}\right)=0$, are due to the cell reflection symmetry of the cell with respect to $z=L/2$. The standard method of solving such problems is to change the integration over the variable z in (10) to integration over θ using eq. (12). The result is the following formula for the applied voltage:

$$V=2\sqrt{\frac{K_1}{\varepsilon_0\tilde{\varepsilon}_a}}\frac{D}{\varepsilon_0\varepsilon_\perp}\frac{L}{V}\int_0^{\theta_{\max}}\left[1-\left(\frac{\varepsilon_a}{\varepsilon_\perp}+\frac{\lambda fd^2v\beta}{\varepsilon_0\varepsilon_\perp}\right)\theta^2\right]\frac{d\theta}{\sqrt{\theta_{\max}^2-\theta^2}}$$

where D is given by (11) with the same change in the integration variable. The Frederiks transition threshold voltage is obtained by taking the limit $\theta_{\max} \to 0$. It is easy to evaluate the integrals, find the limit and obtain:

$$V_{thr} = \pi\sqrt{\frac{K_1}{\varepsilon_0 \tilde{\varepsilon}_a}} = \pi\sqrt{\frac{K_1}{\varepsilon_0 \varepsilon_a + f d^2 v \beta \lambda(\lambda+1)}} \tag{13}$$

We note that, as we expect, in the absence of ferroelectric particles, $f = 0$ and we then recover the classical formula for Frederiks transition threshold voltage [7]:

$$V_{thr}^{\ classical} = \pi\sqrt{\frac{K_1}{\varepsilon_0 \varepsilon_a}} \tag{14}$$

3. ESTIMATES

We use experimental data for ferroelectric particles of $Sn_2P_2S_6$ [6] diluted in the LC mixture ZLI4801 (Merck) to make some estimates. Reznikov *et al* [6] report that their $Sn_2P_2S_6$ colloidal particles possess a spontaneous polarization of 14 μC/cm^2 at room temperature. For the liquid crystal mixture ZLI4801, the dielectric function anisotropy $\varepsilon_a^{LC} = 5.1$. Substituting these parameters into eqs. (13) and (14) yields $V_{thr}^{classical} / V_{thr} \approx 2.7$ for a ferroelectric liquid crystal suspension with particle volume fraction $f = 0.3\ \%$, particle volume $v = 10^{-26} m^3$, and supposing a local field correction factor $\lambda = 1$.

CONCLUSIONS

In this paper we have presented a simple theory of the Frederiks transition in a nematic liquid crystal filled with ferroelectric nanoparticles. In our simple model, in the ferroelectric liquid crystal suspension, the dependence of the angular distortion on the electric field is similar to that in the pure system with effective dielectric function anisotropy given by $\tilde{\varepsilon}_a = \varepsilon_a + \frac{\lambda(\lambda+1) f d^2 v \beta}{\varepsilon_0}$. The theory is consistent with the experimentally observed decrease of electric Frederiks transition threshold voltage [6]. We shall present elsewhere a more complete general effective medium theory for ferroelectric liquid crystal suspension. This theory takes account of the shape, polarizability and local field anisotropy associated with ferroelectric particles.

ACKNOWLEDGMENT

This work has been partially supported by the Royal Society of London through a joint Anglo-Ukrainian cooperation grant.

REFERENCES

[1] Stark, H., *Phys. Rep.* **351**, 387-474 (2001).

[2] Brochard F. and de Gennes P.-G., *J. Physique (France)*, **31**, 691 (1970)

[3] Liang, B.J., Chen, S.-H., *Phys. Rev. A*, **39**, 1441 (1989).

[4] Burylov, S.V. , Zadorozhnii, V.I., Pinkevich, I.P., Reshetnyak, V.Yu. and Sluckin, T.J. *JMMM*, **252,** 153 (2002).

[5] Zadorozhnii, V.I., Vasil'ev, A.N, Reshetnyak, V.Yu., Thomas K.S. and Sluckin, T.J. *Europhysics Lett.* (to be published 2006)

[6] Reznikov, Yu., Buchnev, O., Tereshchenko, O., Reshetnyak, V., Glushchenko, A. and West, J., *Applied Physics Letters*, **82**, 1917-1919, (2003)

[7] de Gennes, P.-G., *The Physics of Liquid Crystals*, Clarendon Press: Oxford, (1974)