Thickness dependence of the anchoring energy of a nematic cell

Original
Thickness dependence of the anchoring energy of a nematic cell / R. M. S., A., Barbero, G., L., K.. - In: JOURNAL OF APPLIED PHYSICS. - ISSN 0021-8979. - 113:(2013), p. 164501. [10.1063/1.4802677]

Publisher:
AIP American Institute of Physics

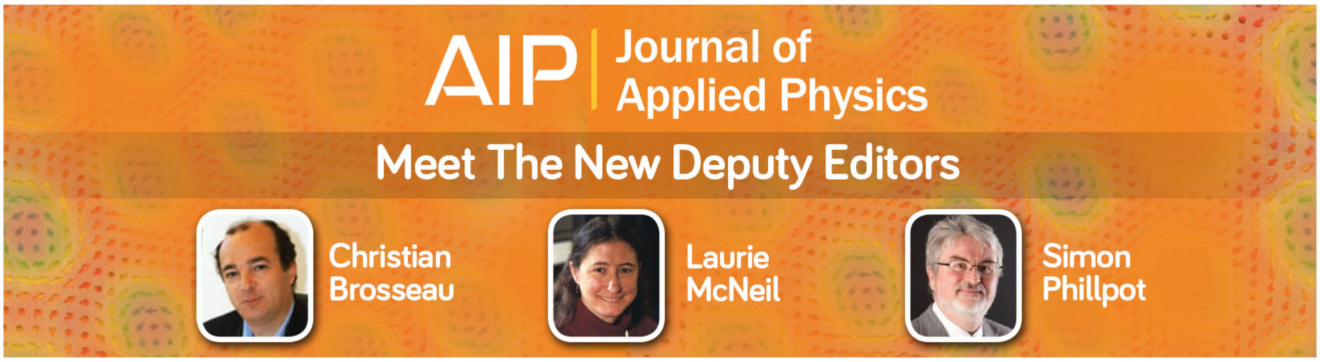
Published
DOI:10.1063/1.4802677

AIP | Journal of Applied Physics

Thickness dependence of the anchoring energy of a nematic cell

R. M. S. Ataalla, G. Barbero, and L. Komitov

Citation: Journal of Applied Physics **113**, 164501 (2013); doi: 10.1063/1.4802677
View online: http://dx.doi.org/10.1063/1.4802677
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/113/16?ver=pdfcov
Published by the AIP Publishing



JOURNAL OF APPLIED PHYSICS **113**, 164501 (2013)

Thickness dependence of the anchoring energy of a nematic cell

R. M. S. Ataalla,[1] G. Barbero,[2] and L. Komitov[1]
[1]*Liquid Crystal Physics, Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden*
[2]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*

(Received 6 February 2013; accepted 8 April 2013; published online 22 April 2013)

The cell gap thickness dependence of the anchoring energy strength of a nematic cell is investigated. The relaxation time of the elastic deformation of a nematic liquid crystal layer imposed by an external electric field is analyzed as a function of the thickness of the nematic layer. The measurements have been performed with conventional sandwich cells with cell gap ranging from 1 μm to 10 μm. According to our data, the anchoring energy strength is not only a characteristic of the interface substrate-nematic liquid crystal but it also depends strongly on the cell thickness. © *2013 AIP Publishing LLC* [http://dx.doi.org/10.1063/1.4802677]

INTRODUCTION

Nematic liquid crystals are anisotropic liquids. Due to their intermolecular interactions, the nematic molecules are aligned along a preferred direction, called director and indicated, usually, by **n**. In the framework of the continuum theory, the elastic energy density of a nematic liquid crystal is a quadratic form of the deformation tensor, built with the spatial derivatives of **n**. In the presence of an external distorting field, the total bulk energy density contains also a term related to the field. If the field is electric, **E**, or magnetic, **B**, the relevant density energy is proportional to $(\mathbf{n}\cdot\mathbf{E})^2$ or to $(\mathbf{n}\cdot\mathbf{B})^2$. The constant of proportionality is related to the dielectric, $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, or diamagnetic, $\chi_a = \chi_\parallel - \chi_\perp$ anisotropy, respectively, where $\parallel$ and $\perp$ refer to **n**. The bulk differential equations describing the nematic distortion field are obtained by minimizing the total energy of the sample, containing a bulk and a surface contribution. The surface contribution is related to the anisotropic part of the surface tension, and it is expected to be a local property, in the sense that it should be independent of the bulk properties.[1] It enters in the problem as boundary conditions for the bulk differential equations.[2] Long time ago, Blinov *et al.*[3] have shown, by analyzing the optical transmission of a nematic cell submitted to a distorting field, that the effective anchoring energy entering in the equilibrium equation is dependent on the thickness. Same results have been obtained by Valenti *et al.*[4] by measuring the thickness dependence of the threshold for the Freedericksz transition in planar samples. However, the results reported in Refs. 3 and 4 were concerning a small number of data, with a small resolution, big errors, and being quite ambiguous. In the present paper, we present a new technique based on the relaxation time of an imposed deformation to investigate the dependence of the effective anchoring energy strength on the thickness of the sample gap, and we show unambiguously that the measurable quantity is not a local property of the interface. We show also that the observed thickness dependence of the anchoring energy strength can be interpreted with a model based on the selective ion adsorption.

EXPERIMENT

The experiments on relaxation time as a function of the cell gap thickness were carried out with conventional sandwich cells. The cells' substrates were prepared in the following way. Polyamic acid SE1211 (Nissan Chem.) dissolved in N-methyl-2-pyrrolidinone with concentration of 5% by weight was spin-coated onto the ITO transparent conductive film deposited on the glass substrates. First at 500 rpm for 10 s and then at 2000 for 20 s. The substrates were prebaked at 100 °C for 3 min to evaporate the solvent, and then baked at 190 °C for 30 min for completing the imidization as prescribed by the manufacturer. The sandwiched cells were assembled with different thicknesses ranging from about 1.5 μm up to 9 μm. Nematic liquid crystal MLC 6608 ($\varepsilon_a < 0$, Merck KGaA, Germany) was injected into the empty cells in the isotropic phase (100 °C). After being slowly cooled down, the cells were inspected for the uniformity of the alignment by means of polarizing microscope with crossed polarizers. The thin polyimide film formed on the top of the ITO layer promoted vertical (homeotropic) alignment. Therefore, the cells appear optically dark. Their electro-optic characteristics were studied in a set-up equipped with polarizing microscope and a photodiode connected to Tektronix TDS 540 digital storage oscilloscope, whose relaxation time is 2 μs. A suitable electric field is applied across the cell in order to induce out of plane transition from vertical to planar alignment. The amplitude of the external applied field is ranging from 2.5 to 3 V/μm. The magnitude of the applied field was chosen to be the one at which the maximum intensity of the light passing through the cell reached the saturation. The frequency of the applied voltage is 10 KHz, to avoid influence of ions on dielectric properties of the nematic liquid crystal. Then, the field is turned off and the optical response was detected by the photodiode. The relaxation time was measured from the optical response as the time corresponding to the time the light 90% of the intensity level dropped to 10%. It was found that the detected electro-optical response has, to a large extent, an exponential character with small deviation from this

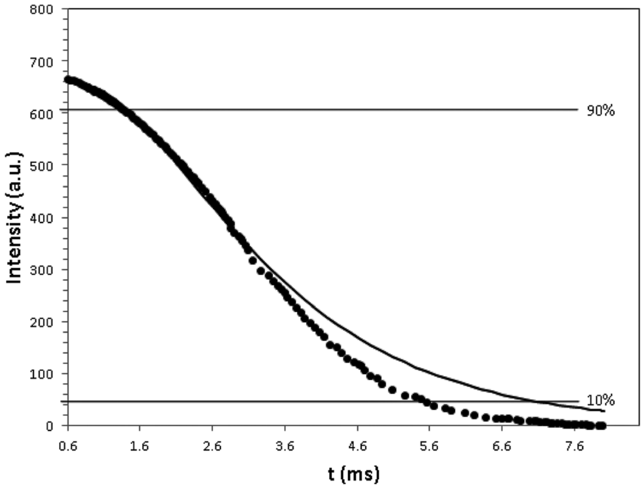


FIG. 1. Time dependence of the transmitted intensity versus T for a cell of thickness $d = 2.7\,\mu$m, for which the measured relaxation time is 3.6 ms. Points, measured. Continuous curve, theoretical prediction evaluated by assuming a single relaxation process with a relaxation time 3.6 ms, and $A = \pi/2$.

character only at the very beginning and the very end of this process, i.e., in the regions where the light intensity is changing from 100% to 90% and from 10% to 0%. In fact, these regions are excluded from our measurements for two reasons. At the beginning of the relaxation, phenomena related to the switch-off of the electric field and to the detection system are important, and responsible for spurious relaxation times. For large observation time, the fact that the system characterized by several multi-relaxation phenomena is observable. Therefore with good approximation, it can be considered that the measured transmitted light intensity decreases exponentially as a function of the time. In Fig. 1, we show the transmitted intensity versus the time t. The dots are the experimental values, whereas the continuous curve is the theoretical prediction by assuming the tilt angle for a simple exponential behavior, with the relaxation time determined as discussed above according to the equation

$$I(t) = I_0 \sin^2\theta(t), \tag{1}$$

since polarizer and analyzer are crossed and when the field is in the on state the sample is nearly planar. In Eq. (1), we assume that $\theta(t) = A\exp(-t/\tau)$, where A is a constant, i.e., that the relaxation is characterized by a single relaxation time. As it follows from Fig. 1, the agreement is rather good in the considered range where the light intensity is changing from 90% to 10%, indicating that in this range the relaxation is well approximated by a simple relaxation phenomenon.

THEORY

Let us consider a nematic cell in the shape of a slab of thickness d. The nematic liquid crystal has $\varepsilon_a < 0$, and the limiting surfaces are treated in such a manner to induce homeotropic alignment. The cartesian reference frame used in our analysis has the z-axis normal to the limiting surfaces at $z = \pm d/2$. The unit vector parallel to the z-axis is $\mathbf{u_z}$. When an external electric field $\mathbf{E} = E\mathbf{u_z}$ is applied to the cell, it induces, if it is larger than the critical field for the Freedericksz transition, an elastic deformation. As well known,[5] the relaxation of the imposed deformation, when the external field is removed, is described by a diffusion equation obtained by equating the elastic torque to the viscous torque that, in the one elastic constant approximation, is

$$k\frac{\partial^2\phi}{\partial z^2} = \eta\frac{\partial\phi}{\partial t}, \tag{2}$$

where k is the average elastic constant, η is the rotational viscosity, and ϕ is the tilt angle formed by $\mathbf{n}$ with $\mathbf{u_z}$. The bulk equation, Eq. (2), is linear. In the simple case where the surface energy is well approximated by the form proposed by Rapini and Papoular,[1] Eq. (2) has to be solved with the boundary conditions

$$\pm k\frac{\partial\phi}{\partial z} + \frac{w}{2}\sin(2\phi) = 0, \tag{3}$$

at $z = \pm d/2$. The assumption that the functional form for the surface energy coincides with the expression of Rapini-Papoular is reasonable also for large deviations from the easy direction, as discussed in Refs. 6 and 7. In the linear limit, Eq. (3) reduces to

$$\pm k\frac{\partial\phi}{\partial z} + w\phi = 0. \tag{4}$$

The solution of Eq. (2) with the boundary conditions given by Eq. (4) is

$$\phi(z,t) = \sum_{n=1}^{\infty} A_n\cos(a_n z)\exp(-t/\tau_n), \tag{5}$$

where the relaxation time τ_n is related to the wave-vector a_n by $\tau_n = (1/a_n^2)(\eta/k)$, as it follows from Eq. (2), and the wave vectors a_n are given by

$$a_n\tan(a_n d/2) = 1/b, \tag{6}$$

where $b = k/w$ is the extrapolation length, as it follows from Eq. (4). The coefficients A_n have to be determined by means of the initial condition of the tilt angle in the presence of the external field, as discussed in Ref. 5.

RESULTS

Experimentally, we are able to determine the shortest relaxation time, τ. In Fig. 2 is reported the dependence of the shortest relaxation time versus the thickness of the cell, $\tau = \tau(d)$. As expected, τ increases with d. In the case of strong anchoring, $w \to \infty$ and hence $b \to 0$. In this case, τ depends on d according to the law

$$\tau = \frac{\eta}{k}\left(\frac{d}{\pi}\right)^2. \tag{7}$$

In fact, in this framework, $\phi(\pm d/2, t) = 0$ and the wave-vectors are $a_n = (2n+1)(\pi/d)$. In Fig. 2, we show the fit of

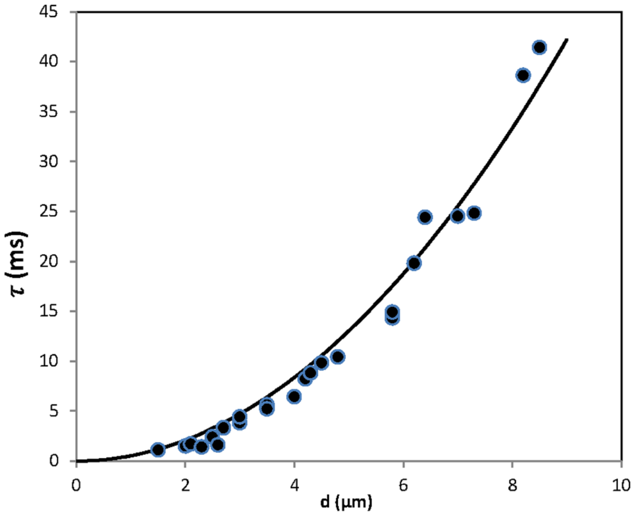


FIG. 2. Dependence of the shortest relaxation time versus the thickness of the cell, $\tau = \tau(d)$. Points are the experimental data and the continuous curve is the best fit obtained with the parabolic law $\tau = c\, d^2$, with $c = 5.2 \times 10^8$ s/m^2.

the experimental data with a law of the type given by Eq. (7), i.e., $\tau = c\ d^2$, where $c = (\eta/\pi^2 k)$. The best fit is obtained with $c = 5.2 \times 10^8$ s/m^2. For the liquid crystal under investigation $k = 1.8 \times 10^{-11}$ N and $\eta = 20 \times 10^{-3}$ Pa s as reported in Refs. 8–10, and hence $c = 1.1 \times 10^8$ s/m^2, a value rather different from the one obtained for the best fit. It follows that the assumption of strong anchoring does not work well for our system. In Fig. 3, we show the experimental data for $\tau = \tau(d)$ and the best fit obtained with the law $\tau = cd^2 + rd$. The parameters of the best fit are $c = 6.4 \times 10^8$ s/m^2 and $r = -8.1 \times 10^2$ s/m. As it is evident from the quoted figure, the fit is good. However, the negative value of r is not compatible with an anchoring energy strength thickness independent. In fact, in the limit of large w but finite, at the lowest order, by considering b as a small parameter, we get $a = (\pi/d) - sb$. By substituting this expression for a in the eigenvalue Eq. (6), and expanding it in power series of b we get $s = 2\pi/d^2$. It follows that, at the first order in b the wave-vector we are looking for is

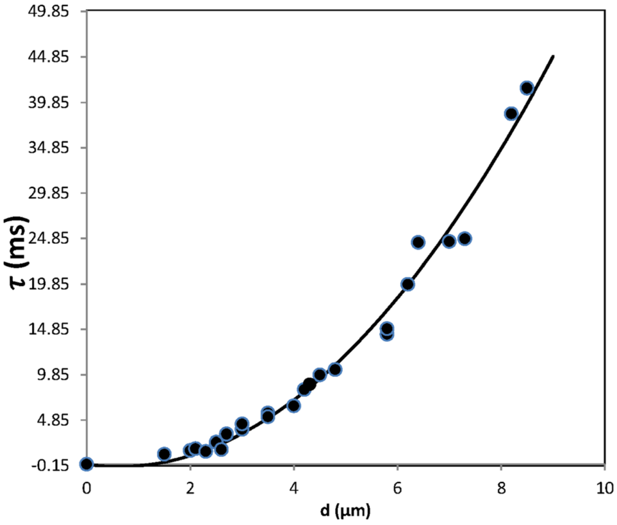


FIG. 3. Dependence of the shortest relaxation time versus the thickness of the cell, $\tau = \tau(d)$. Points are the experimental data and the continuous curve is the best fit obtained with the law $\tau = c\, d^2 + r\, d$, with $c = 6.4 \times 10^8$ s/m^2 and $r = -8.1 \times 10^2$ s/m. The negative value of r is not compatible with the assumption that the surface energy is thickness independent.

$$a = \frac{\pi}{d} - 2\,\frac{\pi}{d^2}\,b. \tag{8}$$

The corresponding relaxation time $\tau = (\eta/k)(1/a^2)$ is then

$$\tau = \frac{\eta}{k}\left(\frac{d}{\pi}\right)^2 + 4\,\frac{\eta}{k}\,\frac{db}{\pi^2}. \tag{9}$$

Equation (9) can be rewritten as

$$\tau = \frac{\eta}{k}\left(\frac{d}{\pi}\right)^2 \frac{d+4b}{d}. \tag{10}$$

As expected, if the anchoring is weak, the thickness d is changed to $d + 2b$.

Equation (9) clearly shows that if the anchoring energy is thickness independent the linear term in d is expected to be positive, contrary to our results. Similar conclusions are derived in Ref. 11. From this result, we conclude that the assumption that the anchoring energy is thickness independent does not work for our case. A possible explanation of the observed thickness dependence of the anchoring energy is the selective adsorption from the limiting surfaces of the ions dissolved in the liquid crystal as well as the flexoelectric properties of this material.[12,13] Using the data for the elastic constant and for the viscosity of the considered liquid crystal, we have evaluated the effective anchoring energy strength $w_{\rm eff}$ by means of Eq. (6), by assuming for τ the relaxation time determined in our experiment. We have

$$w_{\rm eff} = ka\tan(ad/2), \tag{11}$$

where $a = \sqrt{\eta/(k\tau)}$. In the present case, the two limiting surfaces are the same, and the system is submitted to a large electric field, before to relax to the initial undistorted configuration. In this case, by assuming selective adsorption, an electric field of ionic origin, is localized close to the surfaces on a layer whose thickness is of the order of the length of Debye.[14,15] According to Ref. 12, the effective anchoring energy for the nematic cell is

$$w_{\rm eff} = w + \frac{\sigma}{\varepsilon}\left(\frac{\varepsilon_a}{2\varepsilon}\,\lambda\sigma + 2e\right), \tag{12}$$

where $\varepsilon = (2\varepsilon_\perp + \varepsilon_\parallel)/3$ is the average dielectric constant, λ is the length of Debye, related to the ionic surface confinement, $e = e_{11} + e_{33}$ is the flexoelectric coefficient, and σ is the surface density of charge, of ionic origin. As discussed in Ref. 16 $\sigma = \Sigma\, d/(d + 2\lambda)$, where Σ depends on the surface sites available for the ions and on the adsorption energy. The inclusion of the flexoelectric polarization in the surface energy is an important step in revealing the physical mechanisms and the factors responsible for the measurable anchoring energy strength.

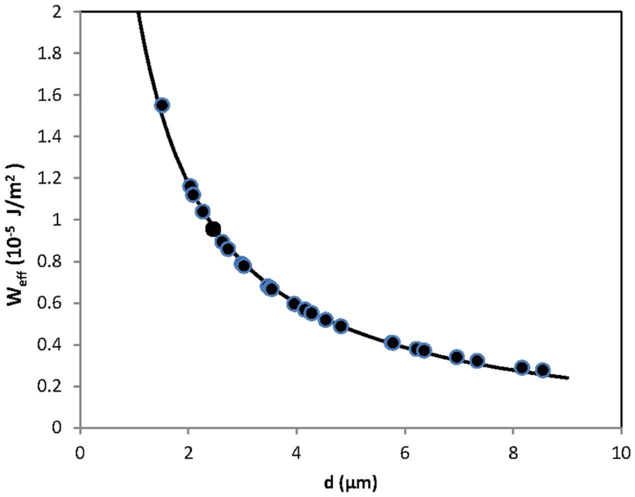


FIG. 4. Dependence of the surface anchoring energy, in the Rapini-Papoular approximation time versus the thickness of the cell, $\tau = \tau(d)$. Points are the experimental data evaluated by means of the eigen-value equation defining the shortest relaxation time, with $k = 1.8 \times 10^{-11}$ N and $\eta = 20 \times 10^{-3}$ Pa s and $\tau = c\,d^2$, with $c = 5.2 \times 10^8$ s/m^2. The continuous curve is the theoretical prediction of the model discussed in the text.

In Fig. 4, we show $w_{\text{eff}} = w_{\text{eff}}(d)$ for the case $\tau = cd^2$. As it is evident from the quoted figures, w_{eff} is a monotonic function of the thickness d. The observed trends are in agreement with the predictions of the model presented in Ref. 12 where surface ionic field and flexoelectric polarization are responsible for the dependence of w_{eff} on d. For the fit, we assume $\varepsilon_{\parallel} = 3.6 \times \varepsilon_0$, $\varepsilon_{\perp} = 7.8 \times \varepsilon_0$, and hence $\varepsilon = 6.4 \times \varepsilon =$ and $\epsilon_a = -4.2 \times \varepsilon_0$,[18] and $\lambda \sim 10^{-7}\,\text{m}$ for the liquid crystal. The parameters of the best fit are $\Sigma = 2.3 \times 10^{-4}\,\text{C/m}^2$, $w = 2.8 \times 10^{-5}\,\text{J/m}^2$, and $e = -8.3 \times 10^{-12}\,\text{C/m}$.[17] As it is evident from the quoted figure, the agreement is rather good in all thickness range. Note that from $\lambda = 10^{-7}\,\text{m}$, it follows that the bulk density of ions is of the order of $n = \varepsilon K_B T/(2\lambda^2 q^2) \sim 9 \times 10^{19}\,\text{m}^{-3}$.[15] The value of the surface charge at saturation is $\sigma \sim nd \sim 2.8 \times 10^{-4}\,\text{C/m}$, for $d \sim 20\ \mu\text{m}$, in good agreement with the parameter of the best fit. We note finally that the conductivity of the liquid crystal, s, is expected of the order of $s \sim 2nq\mu$, where q is the ionic charge and μ the ionic mobility. By assuming $\mu \sim 10^{-9}\,\text{m}^2/(\text{s V})$, typical for ions in a liquid crystal, we get $s \sim 30 \times 10^{-9}\,\text{m}/\Omega$, and hence the resistivity $\rho = 1/s \sim 3 \times 10^{11}\,\Omega/\text{m}$, in agreement with the resistivity of this liquid crystal.[18]

CONCLUSION

We have investigated the thickness dependence of the relaxation time, τ, of an imposed deformation in a nematic cell in the shape of a slab d. Our data $\tau = \tau(d)$ cannot be interpreted by assuming strong anchoring on the limiting surfaces, nor supposing an anchoring energy strength thickness independent. Our experimental results are in good agreement with a model according to which the effective anchoring energy has a bulk contribution related to the selective ionic adsorption responsible for a surface electric field. The surface energy related to this field is partially due to the dielectric anisotropy of the nematic liquid crystal (quadratic in the surface field) and partially to the linear coupling of the surface field with the flexoelectric polarization. From the analysis of the anchoring energy versus the thickness of the cell, we have obtained the bar surface energy, w, the surface density of adsorbed ions, σ, and the flexoelectric coefficient, $e = e_{11} + e_{33}$. Moreover, when the anchoring strength is finite or weak, the relaxation time is also dependent on the anchoring.[5] The stronger is the anchoring the shorter is the relaxation time. Notice that the higher is the purity of the liquid crystal material and the higher is the flexoelectric polarizability, the stronger is the thickness dependence of the anchoring strength and thus the thickness dependence of the relaxation time. Keeping this in mind, we may conclude that for pure liquid crystal materials with high flexoelectric polarizability small changes of the cell gap thickness will result in more efficient reduction of the relaxation time.

[1] A. A. Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach, New York, 1995).
[2] A. Marino, V. Tkachenko, E. Santamato, N. Bennis, X. Quintana, J. M. Oton, and G. Abbate, J. Appl. Phys. **107**, 73109 (2010).
[3] L. M. Blinov, A. Yu. Kabaenkov, and A. A. Sonin, Liq. Cryst. **5**, 645 (1989).
[4] B. Valenti, M. Grillo, G. Barbero, and P. Taverna-Valabrega, Europhys. Lett. **12**, 407 (1990).
[5] A. L. Alexe-Ionescu, G. Barbero, and L. Komitov, Phys. Rev. E **80**, 021701 (2009).
[6] H. Yokoyama and H. A. van Sprang, J. Appl. Phys. **57**, 4520 (1985).
[7] G. Barbero, N. V. Madhusudana, J. F. Palierne, and G. Durand, Phys. Lett. A **103**, 385 (1984).
[8] D. Cuypers, "Vertically aligned nematic liquid crystal microdisplays for projection applications," Ph.D. dissertation (University of Gent, 2004–2005), p. 280.
[9] P. Yeh and C. Gu, *Optics of Liquid Crystal Displays* (John Wiley & Sons, 2009).
[10] H. Kneppe, F. Schneider, and N. K. Sharma, J. Chem. Phys. **77**, 3203 (1982).
[11] X. Nie, R. Lu, H. Xianyu, T. X. Wu, and S.-T. Wu, J. Appl. Phys. **101**, 103110 (2007).
[12] A. L. Alexe-Ionescu, G. Barbero, and A. G. Petrov, Phys. Rev. E **48**, R1631 (1993).
[13] V. G. Nazarenko and O. D. Lavrentovich, Phys. Rev. E **49**, R990 (1994).
[14] V. G. Nazarenko, V. M. Pergamenshchik, O. V. Kovalchuk, A. B. Nych, and B. I. Lev, Phys. Rev. E **60**, 5580 (1999).
[15] P. W. Atkins, *Physical Chemistry*, 5th ed. (Oxford, 2004).
[16] G. Barbero and G. Durand, J. Phys. France **51**, 281 (1990).
[17] P. R. M. Murty, V. A. Ragunathan, and N. V. Madhusudana, Liq. Cryst. **14**, 483 (1993).
[18] Merck KGaA, private communication.