

Deformation of liquid crystal droplets under the action of an external ac electric field

B. I. Lev,¹ V. G. Nazarenko,^{2,*} A. B. Nych,² D. Schur,² P. M. Tomchuk,² J. Yamamoto,¹ and H. Yokoyama^{1,†}
¹Japan Science and Technology Corporation, Yokoyama Nano-structured Liquid Crystal Project, Tsukuba Research Consortium,
 5-9-9 Tokodai, Tsukuba, Ibaraki 300-2635, Japan

²Institute of Physics, National Academy of Science of Ukraine, 46, Prospekt Nauki, 252650, Kyiv-22, Ukraine
 (Received 18 February 2000; revised manuscript received 6 February 2001; published 23 July 2001)

Deformation of liquid crystal droplets suspended in liquid polymer matrix under the action of external electric field was observed in dependence of ion concentration in such system. Experimental dependence of droplet elongation vs electric field demonstrates nonmonotonous character with increase of ion concentration. The theory that provides the basic agreement with experimental observation is developed.

DOI: 10.1103/PhysRevE.64.021706

PACS number(s): 61.30.Gd

I. INTRODUCTION

In recent years there has been an intensive study of heterogeneous systems based on liquid crystals aiming at their potential application in image device. A well-known example of such a system is a polymer dispersed liquid crystal (PDLC) [1–3]. This material consists of nematic droplets embedded in solid polymer matrix. A form of droplets and their spatial distribution are fixed and are defined by many factors during preparation process [4,5]. Investigations in nematic emulsions, i.e., suspensions of LC droplets in a liquid host, allowed for an explicit study of the director configuration inside a single droplet [6,7]. As compared to solid polymer dispersed LCs, nematic colloidal dispersions are much softer since the medium remains a soft matter. As a result, the physics of a colloidal suspensions is much more diverse and complex than the physics of LC droplets in a solid polymer matrix. For instance, droplets can move, interact and change their shape in external fields. One of the mechanisms responsible for droplet form under the action of an external electric field is an electric charge accumulated at the interface between two adjacent substances that have different dielectric constants. When the two substances are both liquids, one of them is dispersed in the other, the classical theory of dielectrics predicts the electrically driven elongation of suspended droplets. Equilibrium deformation will be achieved when the electric and surface forces are balanced and the free energy of the system is minimal. The deformations have already been calculated for nonconducting liquid droplets in insulated media [8–12] as well as for systems, which have sufficient conductivity to effect the electric field distribution around and within the droplets [13–18]. The recent experiments carried out with coexisting nematic-isotropic phases of MBBA and of 5CB showed that observed deformations are many times larger than that found in non-liquid crystal system due to the small interfacial tension. The deformations decrease in amplitude with increasing frequency as a result of the conductivity relaxation of the liquid crystal [19]. However, numerous mechanisms can occur simultaneously and cooperate with an external electric field to

influence the elongation of droplets. To distinguish the mechanisms we performed the measurements of the shape of liquid crystal droplets dispersed in liquid polymer matrix in dependence of ion concentration in such system. Changing the concentration of ions one can follow through the both mechanisms of droplet elongation: pure dielectric for small ion concentration and conductive one for high ion concentration. In the first case the droplet elongates into a spheroid whose long axis coincides with an electric field. Conductive mechanism characterizes by formation of sharp points at the ends of the droplet. While the threshold electric field, the field when droplet starts to elongate, exhibits nonmonotonous behavior with increasing the concentration of ions.

II. EXPERIMENT

The polymer material used in our experiments was a two component mixture of urethane acrylate and tetramethyl oxglycol in weight proportion of 80% and 20%, respectively, [20]. The mixture of polymer and nematic liquid crystal ZhK - 1289 (NIOPIC, Russia) was prepared at the room temperature. Then the dispersion was sandwiched between two glass slides with electrodes, sealed, and loaded into the HS1-i microscope hot stage (Instec Inc.) as it shown in Fig. 1. The

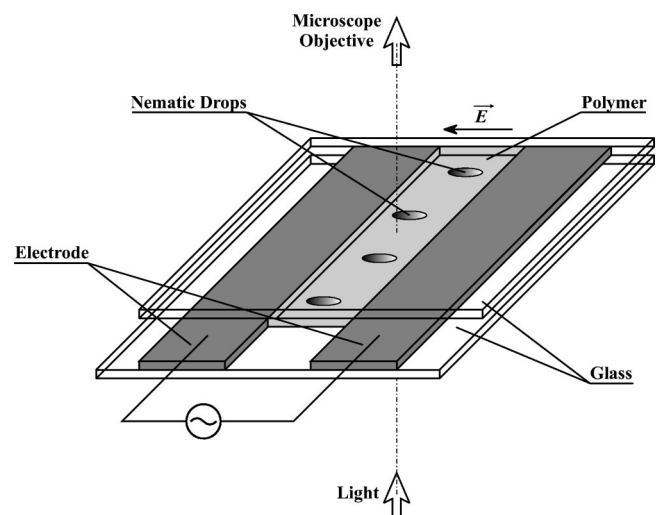


FIG. 1. Scheme of experimental cell.

*Email address: vnazaren@iop.kiev.ua

†Email address: yokoyama@nanols.jst.go.jp

cells differed by concentration of ions. The concentration of ions, n , was estimated from the measurements of the conductivity and mobility of charges [21]. Foreign ionic impurities—molecules of tetrabutyl ammoniumbromide—were added to the liquid crystal. Dissociating, these molecules give additional ions. The form of liquid crystal droplets was changing by application of ac electric field. The experiments were carried out at the fixed temperature of 25°C and droplet size of 40 μm .

For measurements of surface tension of liquid crystal in polymer matrix, two methods were utilized: method of Wilhelmy plate [22] and method of suspended drop [22]. The last methods was modified by very precise pump. To check the reliability of methods we performed measurements of surface tension for pure water—air interface and pure liquid crystal—air interface. The obtained results are in good agreement with those of already reported in literature. Thus, the surface tension of water was obtained as $7.47 \times 10^{-2} \text{ J/m}^2$ and $7.17 \times 10^{-2} \text{ J/m}^2$ for different methods, respectively. The same value reported in Ref. [22] is $7.24 \times 10^{-2} \text{ J/m}^2$. For liquid crystal we obtained $2.62 \times 10^{-2} \text{ J/m}^2$ that is close to the value $2.81 \times 10^{-2} \text{ J/m}^2$ reported in Ref. [23].

III. RESULTS AND DISCUSSION

The liquid crystal dispersed in the polymer mixture forms droplets of a stable spherical form. The size of the droplets depends on concentration of the liquid crystal in polymer matrix. During experiment the droplets do not noticeably move due to quite high viscosity of the polymer. Initial conductivities of the polymer and liquid crystal are $\sigma_p = 4.1 \times 10^{-8} \Omega^{-1} \text{ m}^{-1}$ and $\sigma_{11} = 0.63 \times 10^{-8} \Omega^{-1} \text{ m}^{-1}$, respectively (index $_{11}$ means that conductivity of the liquid crystal was measured along the director). Under the action of ac electric field the droplets elongate in the direction of the field. Changing the ratio between consistent polymer components and adding butylmethacrylate, one can also observe the formation of oblate spheroid. We will limit our consideration only by that case when the droplets deform in the direction of the field. Electric field that corresponds to the beginning of this process is $E_{Cr} = 1.9 \times 10^5 \text{ V/m}$. The shape of a distorted droplet is almost exactly that of a prolate spheroid, see Fig. 2 (*a–c*), unless the electric field reaches the value which corresponds to the instability of the droplets. At this value of electric field, $E_{In} = 7.6 \times 10^5 \text{ V/m}$, the droplets continue to elongate until the break into two smaller ones, which relax into equilibrium state that defined by size of the droplet and applied electric field. Ratio between long and short spheroid droplet axes k as a function of ac electric field is plotted in Fig. 3 (curve *a*). Introducing the foreign ionic impurities into the liquid crystal one can influence the concentration of ions and thus to increase the surface charge that has already existed at the border between liquid crystal and polymer matrix. For the certain concentration of ions, the formation of sharp points at the ends of the droplet was observed, see Fig. 2 (*d–f*). The formation of a spindlelike droplet strongly correlates with the ion concentration in the system. Even for small amount of foreign ionic impurities, that corresponds to the increase in conductivity of polymer

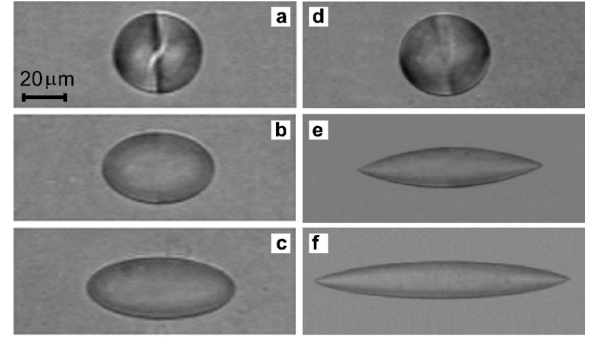


FIG. 2. Liquid crystal droplets under the action of electric field. A,b,c correspond to the pure polymer matrix ($E_a = 0 \text{ V/m}$, $E_b = 5.5 \times 10^5 \text{ V/m}$, $E_c = 7.1 \times 10^5 \text{ V/m}$); d, e, g—are with additional ionic impurities ($E_d = 0 \text{ V/m}$, $E_e = 2.6 \times 10^5 \text{ V/m}$, $E_f = 3.5 \times 10^5 \text{ V/m}$).

on 10%, one can observe the growth of the sharp points. There is no fluid motion associated with final equilibrium form of the droplets. The instability of the droplets becomes also different. When electric field is increased to instability value, small droplets are ejected from the sharp ends of the “mother” droplet.

The values of droplet deformation k for cells that differ by amount of added ionic impurities and thus by their conductivity are plotted in Fig. 3 (curves *b, c, d*). Small increase of ion concentration leads to the sharp decrease of E_{Cr} . Further increase of ion concentration smoothly shifts critical electric field toward the higher value, see Fig. 3.

To understand this phenomenon let us consider a spherical droplet of radius R_0 in a liquid polymer surrounding. In the presence of an ac electric field the form of this droplet will be defined by the minimum of free energy,

$$F = F_D + F_E + F_S. \quad (1)$$

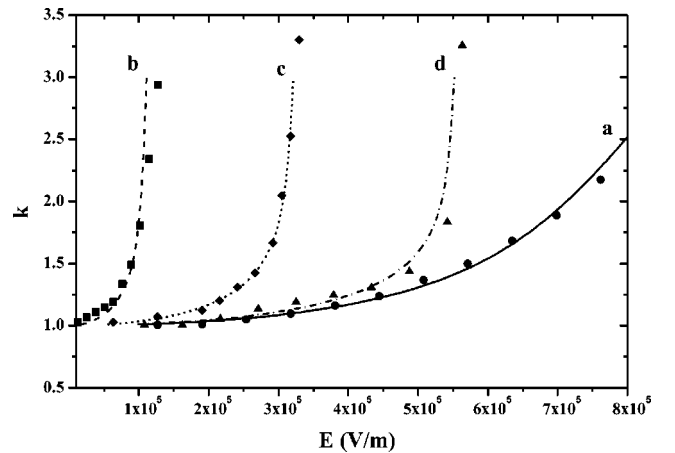


FIG. 3. Electric field dependences of the droplet elongations for different ratios of conductivities between liquid crystal and polymer matrix. The values of the experimentally measured ratios are as follow $\sigma_a = 0.15$, $\sigma_b = 4$, $\sigma_c = 6$, $\sigma_d = 9$. Lines correspond to the theoretical fit by Eq. (11) for curve *a* and by Eq. (14) for curves *b–d*.

F_D is elastic energy of liquid crystal (we assume one constant approximation).

$$F_D = \frac{K}{2} \int dV \{(\operatorname{div} \vec{n})^2 + (\operatorname{rot} \vec{n})^2\}, \quad (2)$$

where K is the elastic constants, \vec{n} is the director. There is an experimental fact that under the action of external electric field the redistribution of liquid crystal director inside the droplet takes place first [24]. When $E \geq K/\Delta\epsilon R^2$ and $\Delta\epsilon > 0$, the director is practically uniformly aligned along the electric field [25]. Further evolution of droplet form is mostly connected to the interaction of electric field with dielectric media of droplet as a whole. So, during process of droplet elongation the director distribution does not sufficiently change. Creation of oblate or prolate spheroid depends only on the ratio of dielectric permittivities of droplet and surrounding materials. Elongation starts when the energy of electric field reaches the value of the surface tension energy. For the case $R > 2K/\Omega$, the anisotropic part of the surface energy is small comparable to the energy of the surface tension and can be neglected in consideration of instability of droplet form. We further will suppose that we are far above the critical electric field for uniform alignment of liquid crystal along the electric field.

F_E is the energy connected with the action of an external electric field:

$$F_E = -\frac{1}{2} \int dV \{ \epsilon_{11} \vec{E}^2 + \Delta\epsilon (\vec{n} \cdot \vec{E})^2 - \epsilon_p E_0^2 \}, \quad (3)$$

where E_0 is the electric field applied to the sample, \vec{E} is the electric field inside the droplet, ϵ_{11} is the dielectric permittivity of the nematic along the director (we consider the electric field is large enough to orient the liquid crystal along the field), $\Delta\epsilon$ is the dielectric anisotropy of the nematic, ϵ_p is the dielectric permittivity of the polymer. The last term in Eq. (3) defines the energy that a droplet could have had if the liquid crystal was substituted by the same material as the droplet surrounding. Electric field inside a droplet or spheroid is uniform, that is the property of any ellipsoid with arbitrary semiaxes [26]. This field can be calculated without exact knowledge of boundary conditions and will be defined by the droplet form as well as by the ratio of dielectric or conductive properties of the both materials, inside the droplet and polymer matrix [26,14]. In general case

$$E = \frac{E_0}{1 + G(X, e)}, \quad (4)$$

were $G(X, e)$ is a factor of depolarization. According to Landau [26]

$$G(X, e) = (X - 1) \frac{1 - e^2}{e^3} (\operatorname{arcthe} e - e), \quad (5)$$

where parameter X is ϵ_{11}/ϵ_p or σ_{11}/σ_p in dependence of dominant process involving in consideration. σ_{11} is the conductivity of the liquid crystal along the director, σ_p is the conductivity of polymer matrix, e being eccentricity of the

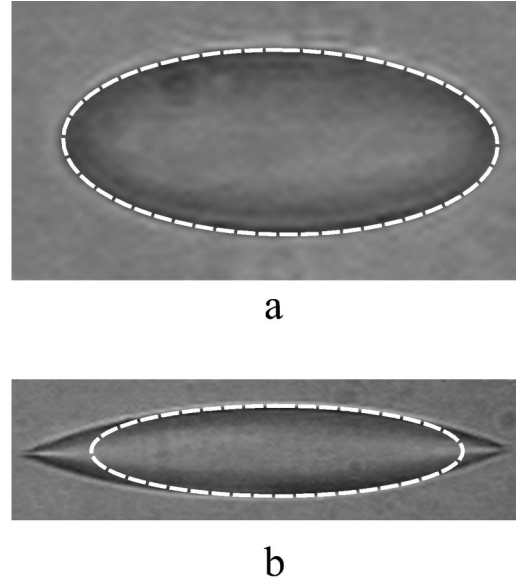


FIG. 4. Computer simulation of droplet form for elliptical (a) and spindlelike (b) droplets. Dashed lines represent computer modeled forms.

deformed droplet. Actually, behavior of a droplet inside a liquid matrix under the action of an external electric field depends on the possibility of redistribution of polarization or real electric charge in a droplet. Interaction of this charge with external electric field creates the force responsible for deformation of a droplet. The value of the deformation depends on elastic and surface properties of the heterogeneous system. Using $e^2 = 1 - R_\perp^2/R_\parallel^2$, where R_\perp and R_\parallel are the length of short and long axis of droplet respectively, and assuming that the droplet becomes really elliptical (we have experimental evidence of this fact, see Fig. 4) one can define the coordinates of deformed droplet surface as follow:

$$r = \frac{R_\perp}{[1 - e^2 \cos^2 \theta]^{1/2}}, \quad (6)$$

where θ is the angle between radius vector to a point on the droplet surface and direction of electric field. According to [13], one can write F_E as follow,

$$F_E = -\frac{\epsilon_p E_0^2 R_\perp^2 R_\parallel (\epsilon - 1)}{6[1 + G(\epsilon, e)]^2}, \quad (7)$$

where $\epsilon = \epsilon_{11}/\epsilon_p$.

F_S is the surface free energy due to the interface between two different media,

$$F_S = \oint (\Omega + W) dS + \oint W(\vec{\nu} \cdot \vec{n})^2 dS, \quad (8)$$

where Ω is isotropic part of the surface tension, W is anisotropic one, $\vec{\nu}$ is the normal to the surface. Since the $W \ll \Omega$, for spheroid droplet we have

$$F_S = 2\pi\Omega R_\perp^2 \left(1 + \frac{R_\parallel}{R_\perp} \frac{\arcsin e}{e} \right). \quad (9)$$

The total free energy follows from Eqs. (2), (3), and (9) as

$$F = 2\pi\Omega R_{\perp}^2 \left(1 + \frac{R_{\parallel}}{R_{\perp}} \frac{\arcsin e}{e} \right) - \frac{\varepsilon_p E_0^2 R_{\perp}^2 R_{\parallel} (\varepsilon - 1)}{6[1 + G(\varepsilon, e)]^2}. \quad (10)$$

To find the final steady form of droplets we have to minimize the above free energy with the condition that volume of droplet is the same for the time of experiment, $4/3\pi R_{\perp}^2 R_{\parallel} = 4/3\pi R_0^3$, where R_0 is initial droplet size. Finally, one has minimum of Eq. (10) on deformation parameter $k \equiv R_{\parallel}/R_{\perp}$,

$$-\frac{2}{3}k^{-5/3} + \frac{4}{3} \frac{k^{1/3}C}{A} + \frac{k^{1/3}}{A^2} - \frac{k^{7/3}C}{A^3} + [3kA - (2k^2 + 1)B] \frac{wA^4}{\left(kB + \frac{k^2 - \varepsilon}{\varepsilon - 1}A \right)^3} = 0, \quad (11)$$

where we use the following abbreviation: $A \equiv \sqrt{k^2 - 1}$, $B \equiv \operatorname{arctanh} \sqrt{(k^2 - 1)/k^2}$, $C \equiv \arcsin \sqrt{(k^2 - 1)/k^2}$ and

$$w = \frac{\varepsilon_p E_0^2 R_0}{6\pi\Omega} \quad (12)$$

is the Taylor parameter, that is defined by the ratio between electric and surface energies of the droplet with radius R_0 .

For the case when the both, polarization and conductive properties, take place in the process of redistribution of electric charges, the electric free energy of a droplet inside an isotropic matrix, has the known solution [13,14]:

$$F_E = \frac{\varepsilon_p E_0^2 R_0^3}{6[1 + G(\sigma, e)]} \left\{ \frac{\varepsilon - \sigma}{1 + G(\sigma, e)} - (\sigma - 1) \right\}, \quad (13)$$

where $\varepsilon = \varepsilon_{11}/\varepsilon_p$, $\sigma = \sigma_{11}/\sigma_p$ and $G(\sigma, e)$ is defined by Eq. (5).

Now one can find the equation that describe the steady state of the droplet under the action of electric field:

$$-\frac{2}{3}k^{-5/3} + \frac{4}{3} \frac{k^{1/3}C}{A} + \frac{k^{1/3}}{A^2} - \frac{k^{7/3}C}{A^3} = \frac{w}{[1 + G(\sigma, e)]^3} \frac{\partial G}{\partial k} \{ 2(\varepsilon - \sigma) - (\sigma - 1)[1 + G(\sigma, k)] \}. \quad (14)$$

Finally, from Eq. (11) we can analyze the experimental dependence of droplet deformation on the value of applied

electric field without additional ionic impurities. The theoretical dependency is represented in Fig. 3 (curve *a*) by solid lines. The best fitting was obtained for the values of ε and Ω_a as 3.12 and 1.55×10^{-3} J/m², respectively. We have also experimentally measured ε and obtained similar value, $\varepsilon = 3.17$. For the case when additional ionic impurities were added, dependence $k(E)$ is approximated by Eq. (14) with the following parameters: $\Omega_b = 0.14 \times 10^{-3}$ J/m², $\Omega_c = 1.5 \times 10^{-3}$ J/m², $\Omega_d = 4.9 \times 10^{-3}$ J/m², $\sigma_b = 8$, $\sigma_c = 10$, $\sigma_d = 11$. Index letters at the Ω and σ mean their correspondence to the curve in Fig. 3. To provide the basic agreement with experiments we have to suppose nonmonotonic behavior of the surface tension with increasing the concentration of ions in the system. The nonmonotonic behavior of surface tension can be caused by ion adsorption at the surface resulting in creation of double electric layer as it was considered in [27,28]. For the high ion concentration the surface tension is mostly governed by the value of double electric layer. Experimentally measured surface tensions for pure materials and for all ion concentrations used in experiment on droplet elongation are $\Omega_a = 3.3 \times 10^{-3}$ J/m², $\Omega_b = 2.16 \times 10^{-3}$ J/m², $\Omega_c = 2.3 \times 10^{-3}$ J/m², $\Omega_d = 2.93 \times 10^{-3}$ J/m². The discrepancies that arise between experimental and theoretical values can be attributed to the method of measurement of the surface tension. The experiments were performed for a flat surface while the calculated value is related to small droplets dispersed in polymer matrix which are subjected to the action of an external electric field. In the latter case the effective electric field applied directly to droplets differs from that of applied to the cell due to polarization effects. Nevertheless, one can point out the similar tendency of both sets of data to have minimum for some concentration of added ionic impurities. The experimentally measured ratios of conductivity (the experiments were performed separate for liquid crystal and polymer) are $\sigma_b = 4$, $\sigma_c = 6$, $\sigma_d = 9$. For these data one can see the satisfactory agreement between the theory and experiment.

To summarize, the nematic liquid crystal droplets suspended in liquid polymer matrix elongate under the action of external electric field. Ionic impurities inserted into the system strongly affect the form and the value of the deformation via changes of the surface tension between the liquid crystal and polymer matrix. Theoretical model, based on redistribution of polarized and free electric charges, shows good quantitative agreement with the experimentally observed deformations.

ACKNOWLEDGMENTS

This work was supported by STCU Grant No. 637 and INTAS Grant No. 30234. We thank A. M. Gabovich, A. I. Voitenko, and O. D. Lavrentovich for helpful discussion.

- [1] J. W. Doane, *Liquid Crystals: Applications and Uses*, edited by B. Bahadur (World Scientific New Jersey 1990), Vol. **1**, Chap. 14, p. 362.
 [2] J.W. Doane, N.A. Vaz, B.G. Wu, and S. Zumer, *Appl. Phys. Lett.* **48**, 269 (1986).

- [3] S. Zumer and J.W. Doane, *Phys. Rev. A* **34**, 3373 (1986).
 [4] N.A. Vaz, G. Smith, and G.P. Montgomery, *Mol. Cryst. Liq. Cryst.* **146**, 1 (1987).

- [5] G.V. Smith and N.A. Vaz, *Liq. Cryst.* **3**, 543 (1988).
- [6] O.D. Lavrentovich and E.M. Terent'ev, *Zh. Éksp. Teor. Fiz.* **91**, 2084 (1986) [*Sov. Phys. JETP* **64**, 1237 (1986)].
- [7] G.E. Volovik and O.D. Lavrentovich, *Zh. Éksp. Teor. Fiz.* **85**, 1997 (1983) [*Sov. Phys. JETP* **58**, 1159 (1983)].
- [8] C.G. Garton and Z. Krasucki, *Proc. R. Soc. London, Ser. A* **280**, 211 (1964).
- [9] G.I. Taylor, *Proc. R. Soc. London, Ser. A* **280**, 383 (1964).
- [10] R.S. Allan and S.G. Masson, *Proc. R. Soc. London, Ser. A* **267**, 62 (1962).
- [11] G.I. Taylor, *Proc. R. Soc. London, Ser. A* **291**, 145 (1966).
- [12] G.I. Taylor, *Proc. R. Soc. London, Ser. A* **291**, 159 (1966).
- [13] S.N. O'Konski and H.C. Thacher, *J. Phys. Chem.* **57**, 955 (1953).
- [14] S.N. O'Konski and F.E. Harris, *J. Phys. Chem.* **61**, 1172 (1957).
- [15] S.I. Shchukin and A.I. Grigor'ev, *Zh. Tekh. Fiz.* **69**, 23 (1999) [*Tech. Phys.* **44**, 758 (1999)].
- [16] S.I. Shchukin and A.I. Grigor'ev, *Zh. Tekh. Fiz.* **69**, 49 (1999) [*Tech. Phys.* **44**, 913 (1999)].
- [17] A.I. Grigor'ev, *Zh. Tekh. Fiz.* **55**, 1272 (1985) [*Sov. Phys. Tech. Phys.* **30**, 736 (1985)].
- [18] S.O. Shiryayeva and A.I. Grigor'ev, *Zh. Tekh. Fiz.* **66**, 12 (1996) [*Tech. Phys.* **41**, 1220 (1996)].
- [19] Ch.S. Park, N.A. Clark, and R.D. Noble, *Phys. Rev. Lett.* **72**, 1838 (1994).
- [20] V.G. Nazarenko, S. Sarala, and N.V. Madhusudana, *Jpn. J. Appl. Phys.* **33**, 2641 (1994).
- [21] N.I. Gritsenko and N.V. Moshel, *Ukr. Fiz. Zh. (Russ. Ed.)* **25**, 1815 (1980).
- [22] A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1976).
- [23] V. N. Matveenko and E. A. Kirsanov, *Surface Phenomena in Liquid Crystals* (MGU, Moscow, 1991).
- [24] A. Golemme, S. Zumer, J.W. Doane, and M.E. Neubert, *Phys. Rev. A* **37**, 559 (1988).
- [25] B.G. Wu, J.E. Erdmann, and J.W. Doane, *Liq. Cryst.* **5**, 1453 (1989).
- [26] L. D. Landau and E. M. Lifshits, *Electrodynamics of Soft Matter* (Nauka, Moscow, 1976).
- [27] A.M. Gabovich and A.I. Voitenko, *Electrochim. Acta* **28**, 1771 (1983).
- [28] A.M. Gabovich and A.I. Voitenko, *Electrochim. Acta* **35**, 545 (1990).