

A Study of Polarization in Smectic Liquid Crystals via Statistical-Physics Methods

E. S. Filimonova^{a*}, A. V. Emel'yanenko^{a**}, and J. H. Liu^b

^a Faculty of Physics, Moscow State University, Moscow, 119991 Russia

^b Faculty of Chemical Engineering, National University, Tainan, 70101 Taiwan

*e-mail: filimonova@polli.phys.msu.ru,

**e-mail: emel@polly.phys.msu.ru

Received September 13, 2016; in final form, October 20, 2016

Abstract—The spontaneous polarization processes in synclinic and anticlinic smectic liquid crystals are discussed in the context of molecular statistical theory. The effects of interaction between molecules, external electric fields, and bending of molecules via polarization are elucidated as well.

Keywords: liquid crystals, smectics, ferroelectricity.

DOI: 10.3103/S0027134917040063

INTRODUCTION

Liquid crystals (LCs) are unique materials that can exhibit properties intermediate between a liquid and solid due to the anisotropic structures of the molecules (such as molecules stretched out like a stick) [1, 2]. The best-known LC states are presented by nematic and smectic phases. In a nematic phase, the molecular mass centers are randomly distributed by analogy with a liquid, but the molecules have a predominant orientation. The direction of the predominant orientation of the long axes in these molecules is called the director. In smectic phases, the molecules are agglomerated in layers; in other words, long-range translation order exists in a certain direction. The inclined smectic phases (when the director direction and the normal to the smectic layer plane are different) can possess polar ordering of the so-called short molecular axes (perpendicular to elongation of the molecule). This results in spontaneous polarization [3–5]. Since all LC molecules are very sensitive to various external effects, such as electric and magnetic fields and admixtures, liquid crystals can be applied in different sensors for detection of impurities or external fields [6–9]. The LC structure (distribution of director and or/polarization in space, as well as oriented ordering of the long/short molecular axes) changes under the external conditions, which allows visualization of the external effects. The present work is thus dedicated to studying one of the order parameters, that is, the degree of polar ordering of molecules (polarization), in synclinic and anticlinic smectic phases, the molecular aspects of its occurrence, and the influ-

ence of external electric fields on the structure of the above phases.

Meyer, who established and investigated ferroelectricity in liquid crystals [10, 11], explained the occurrence of spontaneous polarization in chiral smectics by the presence of a polar axis in the direction perpendicular to the plane of inclination of molecules in smectic layers. If chiral molecules possess dipoles they are oriented predominately along the polar axis.

Typically in theoretical works, spontaneous polarization is considered in the context of phenomenological theory and no molecular aspects of its emergence are taken into account. In [12–17], spontaneous polarization was described at the molecular level, while the molecular dipole distribution was finally obtained by decomposition of the polarization components into Taylor series; the role of molecular theory was thus reduced to the definition of coefficients in the phenomenological theory. At the same time, the simplest inclined synclinic and anticlinic smectic phases allow one to avoid this decomposition and to find the molecular dipole distribution via a method identical to the Maier–Saupe theory [18, 19] in order to establish the distribution of long molecular axes in a nematic.

A smectic is called synclinic [1, 2] if the director possesses the same orientation in all layers (Fig. 1a). In contrast, in an anticlinic smectic the direction of the director inclination alternates from layer to layer, remaining in the same plane (Fig. 1b).

When studying liquid-crystal structures at the molecular level, it is essential to draw attention to sym-

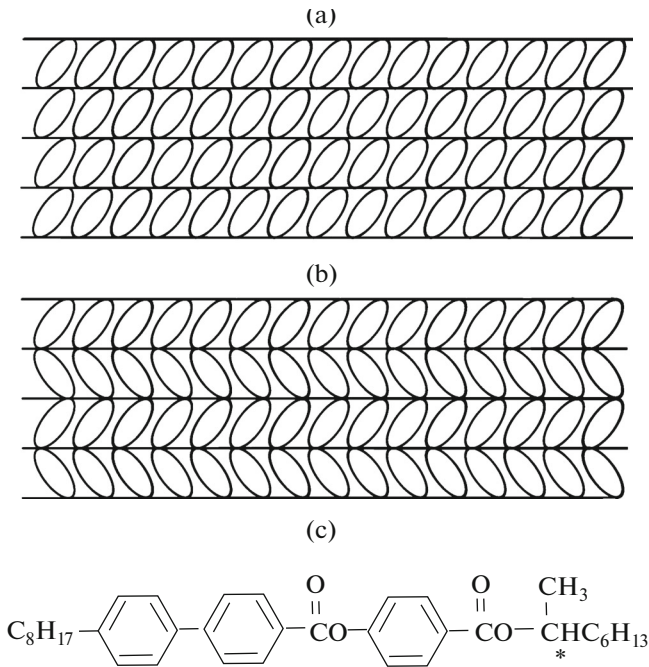


Fig. 1. (a) Synclinic and (b) anticlinic smectic liquid crystals; (c) MNRVS molecule.

metry features of molecules, thus, primitive geometric objects in the form of hard rods, pears, bananas, hockey sticks, and other shapes with simple electric charge distributions (i.e., dipole moments) are often taken for consideration. Many molecules have no symmetry planes (such as a bent molecule with a dipole perpendicular to the bending direction); this property is called chirality [1]. One example is the MNRVS system, where the dipole moment is coupled with a CH–CH₃ group and the symbol * denotes the chirality center (Fig. 1c).

This work is aimed at elucidating the effects of various types of molecular interaction on the polarization in synclinic and anticlinic smectic liquid crystals via statistical physics methods.

1. MOLECULAR STATIC THEORY

Let us consider a liquid crystal that satisfies the following conditions: the molecular mass centers are in the plane of smectic layers, the long axes of molecules are oriented along the director direction \mathbf{n} in each smectic layer, and each molecule possesses a transverse (i.e. perpendicular to its long axis) electric dipole $\boldsymbol{\mu}$. As was shown by Meyer, the polarization \mathbf{P} must be perpendicular to vectors \mathbf{n} and \mathbf{k} , i.e., be normal to the layer surface (Fig. 2). Let ψ be the angle between the transverse dipole moment of the arbitrary molecule and the polarization vector direction.

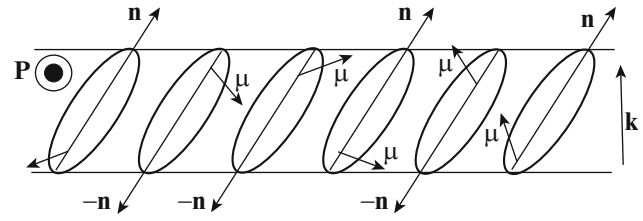


Fig. 2. Biaxial molecules within a layer.

The polarization in a smectic layer i can be written as [20]:

$$\mathbf{P}_i = \rho \int_0^{2\pi} \boldsymbol{\mu}_i f_i(\psi) d\psi, \quad (1)$$

where ρ is the density of molecules in the layer and $f_i(\psi)$ is the distribution function of the ψ orientations of dipoles $\boldsymbol{\mu}$ in a layer i relative to the direction \mathbf{P}_i .

In order to find the dipole distribution function, the expression for free energy of the unit volume has to be reduced, which has the following form for biaxial molecules with a fixed long-axis direction [20]:

$$F = \rho k_B T \sum_{i=1}^N f_i(\psi_1) \ln f_i(\psi_1) d\psi + \frac{1}{2} \rho^2 \times \sum_{i,j=1}^N f_i(\psi_1) f_j(\psi_2) g_{ij}(\mathbf{r}_\perp) U_{ij}(\mathbf{r}_\perp, \psi_1, \psi_2) d^2 \mathbf{r}_\perp d\psi_1 d\psi_2, \quad (2)$$

where T is the temperature, k_B is the Boltzmann constant, N is the number of smectic layers, and U_{ij} is the total potential of interaction between the molecule in a layer i and the molecule in a layer j . Here, $g_{ij}(\mathbf{r}_\perp)$ describes the correlation of the positions of these molecules and \mathbf{r}_\perp is the projection of the intermolecular vector onto the layer plane. The first term in Eq. (2) describes the orientation entropy and the second is related to the internal energy of the system.

Minimization of the expression for free energy (2) results in the following distribution function of short molecular axes:

$$f_i(\psi) = \frac{1}{I} \exp \left\{ -\frac{\rho}{k_B T} U_{MF}^{(i)}(\psi) \right\}, \quad (3)$$

$$I = \int_0^{2\pi} \exp \left\{ -\frac{\rho}{k_B T} U_{MF}^{(i)}(\psi) \right\} d\psi, \quad (4)$$

where U_{MF} is the average field that acts on the molecule in the layer i :

$$U_{MF}^{(i)}(\psi) = \sum_{j=1}^N \int f_j(\psi_2) g_{ij}(\mathbf{r}_\perp) U_{ij}(\mathbf{r}_\perp, \psi_1, \psi_2) d^2 \mathbf{r}_\perp d\psi_2. \quad (5)$$

A further consideration will occur for a case of strong correlation of molecules inside each layer $g_{ii}(\mathbf{r}_\perp)$ and in the adjacent layers $g_{i,\pm 1}(\mathbf{r}_\perp)$ when the integral over the vector \mathbf{r}_\perp can be taken by the saddle-point method. Thus, the integral over the vector \mathbf{r}_\perp in formula (5) for $j = i$ can be replaced by the product $\langle g_{ii} \rangle \int_0^{2\pi} U_{i,i}(\varphi, \psi_1, \psi_2) d\varphi$, where the unique angle φ describes the mutual arrangement of elongated molecules in side-by-side contact, and for $j = i \pm 1$ —by $\langle g_{i,i\pm 1} \rangle U_{i,i\pm 1}(\psi_1, \psi_2)$. As well, one can assume that only the neighboring molecules interact with each other, then $\rho \langle g_{ii} \rangle = \rho \langle g_{i,i\pm 1} \rangle = 1$ and the molecular interactions in more distant layers ($|j - i| > 1$) be neglected.

2. THE MECHANISM OF SPONTANEOUS PIEZOELECTRIC POLARIZATION IN AN INCLINED SMECTIC

As the simplest model bent molecule, let us consider a hockey-stick model, which is asymmetric relative to either the long molecular axis \mathbf{a} (Fig. 3a) and the short molecular axis \mathbf{b} (Fig. 3b). The bent shape itself means that no chirality occurs, because the plane of axes \mathbf{a} and \mathbf{b} can be a symmetry plane. However, if the molecule exhibits a dipole moment that is different in its orientation from axes \mathbf{a} and \mathbf{b} , it can be considered as chiral. It is known that in real smectic liquid crystals the directions of the long \mathbf{a} and $-\mathbf{a}$ axes are equiprobable; the qualitative description will thus necessitate a transverse dipole moment (perpendicular to the long axis \mathbf{a}). Since the transverse dipole moment component along axis \mathbf{b} itself does not cause chirality, the qualitative description will therefore be based on the dipole moment (or its projection) perpendicular to both the long axis \mathbf{a} and the short axis \mathbf{b} . Let the unit vector along this direction be called axis $\mathbf{c} = [\mathbf{a} \times \mathbf{b}]$. We will show in the context of molecular theory how the bent shape of a molecule (its asymmetry relative to axes \mathbf{a} and \mathbf{b}) can cause the alignment of axes \mathbf{c} of molecules in the direction perpendicular to the molecule inclination plane in a smectic layer, polarization in the inclined smectic layer, and influence the polarization. This peculiarity of molecular geometry is that the effective potential of interaction of arbitrary molecules 1 and 2 that are in the same smectic layer must include a term that is polar in both directions \mathbf{a} and \mathbf{b} of each molecule. The simplest example of this term can be written as

$$U_{12} = c_p(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{b}_1 \cdot \mathbf{u}_{12}) + c_p(\mathbf{a}_2 \cdot \mathbf{u}_{12})(\mathbf{b}_2 \cdot \mathbf{u}_{12}), \quad (6)$$

where c_p is a piezoelectric constant that depends on the degree of bending of the molecule, $\mathbf{u}_{12} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$ is the unit vector connecting molecules 1 and 2 within a layer, \mathbf{a}_1 and \mathbf{a}_2 are the vectors that determine the

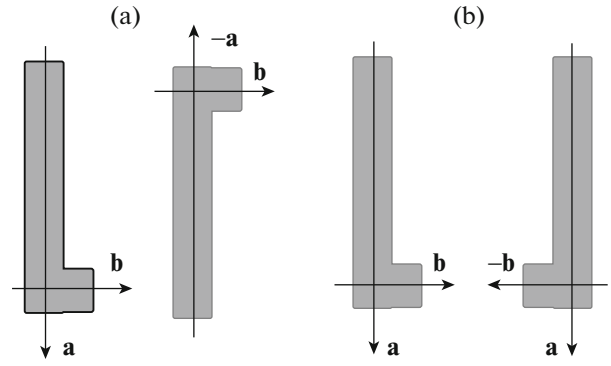


Fig. 3. The asymmetry of a bent molecule relative the changes in orientations: (a) \mathbf{a} by $-\mathbf{a}$; (b) \mathbf{b} by $-\mathbf{b}$.

directions of long axes in molecules 1 and 2, and \mathbf{b}_1 and \mathbf{b}_2 are the vectors that define the directions of the short axes in molecules 1 and 2. The \mathbf{b} vector can be presented as $\mathbf{b} = -[\mathbf{a} \times \mathbf{c}]$. Then

$$\begin{aligned} (\mathbf{b}_1 \cdot \mathbf{u}_{12}) &= -([\mathbf{a}_1 \times \mathbf{c}_1] \cdot \mathbf{u}_{12}) = ([\mathbf{a}_1 \times \mathbf{u}_{12}] \cdot \mathbf{c}_1), \\ (\mathbf{b}_2 \cdot \mathbf{u}_{12}) &= -([\mathbf{a}_2 \times \mathbf{c}_2] \cdot \mathbf{u}_{12}) = ([\mathbf{a}_2 \times \mathbf{u}_{12}] \cdot \mathbf{c}_2), \end{aligned} \quad (7)$$

where \mathbf{c}_1 is a vector orthogonal to \mathbf{a}_1 and \mathbf{b}_1 , and \mathbf{c}_2 is a vector orthogonal to \mathbf{a}_2 and \mathbf{b}_2 . Thus,

$$U_{12} = c_p(\mathbf{a}_1 \cdot \mathbf{u}_{12})([\mathbf{a}_1 \times \mathbf{u}_{12}] \cdot \mathbf{c}_1) + c_p(\mathbf{a}_2 \cdot \mathbf{u}_{12})([\mathbf{a}_2 \times \mathbf{u}_{12}] \cdot \mathbf{c}_2). \quad (8)$$

Let us average the U_{12} potential over the orientation of the intermolecular vector \mathbf{u}_{12} in the plane of a smectic layer and remember that $\mathbf{a}_1 \parallel \mathbf{a}_2 \parallel \mathbf{n}$:

$$\langle U_{12} \rangle \sim -c_p(\mathbf{n} \cdot \mathbf{k})[\mathbf{n} \times \mathbf{k}](\mathbf{c}_1 + \mathbf{c}_2). \quad (9)$$

Based on the polarization defined by Eq. (1) and formula (3) for the distribution function of short molecular axes, we obtain:

$$\mathbf{P} = \frac{\rho \mu}{I} \int_0^{2\pi} \boldsymbol{\mu} \exp \left\{ \frac{c_p}{\mu k_B T} (\mathbf{n} \cdot \mathbf{k}) ([\mathbf{n} \times \mathbf{k}] \cdot \boldsymbol{\mu}) \right\} d\psi, \quad (10)$$

$$\text{where } I = \int_0^{2\pi} \exp \left\{ \frac{c_p}{\mu k_B T} (\mathbf{n} \cdot \mathbf{k}) ([\mathbf{n} \times \mathbf{k}] \cdot \boldsymbol{\mu}) \right\} d\psi.$$

As was shown by Meyer, owing to symmetry, spontaneous polarization may occur only in the direction $[\mathbf{n} \times \mathbf{k}]$; i.e., in the direction normal to the plane of inclination (Fig. 2). The polarization will then be determined as

$$P = \frac{\rho \mu}{I} \int_0^{2\pi} \cos \psi \exp \left[\frac{c_p}{2k_B T} \sin(2\theta) \cos \psi \right] d\psi, \quad (11)$$

$$\text{where } I = \int_0^{2\pi} \exp \left[\frac{c_p}{2k_B T} \sin(2\theta) \cos \psi \right] d\psi,$$

where θ is the angle of molecular inclination in a smectic layer (the angle between the \mathbf{n} and \mathbf{k} directions). As follows from formula (11), the reduced polarization $P/(\rho\mu)$ plays the role of the order parameter, for which the value depends on the angle of inclination θ and the piezoelectric constant c_p .

3. THE EFFECT OF DIPOLE–DIPOLE INTERACTION ON THE POLARIZATION IN SYNCLINIC AND ANTICLINIC SMECTIC PHASES

In accordance with a model problem defined in Section 1, we have to take the dipole–dipole interaction of molecules within a layer into consideration, as well as the dipole–dipole interaction of molecules in the adjacent layers. For molecules within a layer, we write the dipole interaction potential and average it over the radius-vector \mathbf{r}_{12} , which connects molecule 1 with its nearest neighbors and corresponds to the strong correlation $\mathbf{g}_i(\mathbf{r}_1)$ between the nearest molecules. By and large, in the case of an inclined smectic the radius-vector will be described with an ellipse. Nevertheless, for small angles of inclination the ellipticity is low and it can be shown that the contribution of the latter to the average potential is proportional to the second degree of the angle θ . Let us confine ourselves to the terms with the first degree of the angle θ . This is equivalent to the dipole–dipole interaction in a non-inclined smectic where all nearest neighbors of a molecule are located on the circle. Thus, we obtain

$$\begin{aligned} & \oint_0^{2\pi} \Delta U_{ii}^{\mu\mu}(\varphi, \psi_1, \psi_2) d\varphi \\ &= \oint_0^{2\pi} \left[\frac{(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2)}{r_{12}^3} - 3 \frac{(\boldsymbol{\mu}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12})}{r_{12}^5} \right] d\varphi \approx -\frac{3}{d^3} (\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2), \end{aligned} \quad (12)$$

for the average dipole–dipole interaction, where d is the width of the molecule, and where in the spirit of the reasoning about the nearest neighbors in Section 1, we considered it appropriate to replace 2π by 6.

Let us now focus on the dipole–dipole interaction of molecules in the neighbor smectic layers.

A strong correlation between molecules in the neighboring smectic layers correlates with their arrangement strictly one above the other, when the vector \mathbf{r}_{12} is parallel to the normal to the plane of smectic layers \mathbf{k} . Therefore, the dipole–dipole potential is written as

$$\Delta U_{i,i\pm 1}^{\mu\mu}(0, \psi_1, \psi_2) = \frac{1}{h^3} (\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2), \quad (13)$$

where h is the average distance between the dipoles of molecules in the adjacent layers.

We will generalize the recurrent relationship for polarization (11), taking the dipole–dipole interactions into account in the bulk of each smectic layer (12) and in the neighboring smectic layers (13). Since the transverse dipole associated with the chiral center is located at only one of two ends of the elongated molecule (see Fig. 2), it will be close for only a half of the side neighbors for each molecule in the layer i . Thus, a term (12) will enter the average field with a factor of 1/2.

The same is true for the upper or lower neighbors for the molecule with layer i , where the transverse dipole is close to either the upper layer or the lower one; thus, the term (13) will also enter the average field with the multiplier 1/2. It is evident that the dipole–dipole interaction in the neighbor layers will exert a different influence on the polarization in synclinic and anticlinic smectic phases. For a synclinic smectic with polarization equal in all layers we have:

$$\begin{aligned} p &= \frac{1}{I} \int_0^{2\pi} \cos \psi \exp \left\{ \left[\tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3 - \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi, \\ \text{where } I &= \int_0^{2\pi} \exp \left\{ \left[\tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3 - \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi. \end{aligned} \quad (14)$$

and where $\tilde{c}_p = c_p/k_B T$, $\mu_{\text{ef}} = \mu/\sqrt{k_B T d^3}$, and the magnitude $p = P/(\rho\mu)$ plays the role of the polar order parameter (being from zero to one), as it equals the polarization per molecule, in relation to its dipole moment.

In the anticlinic smectics, where the polarization changes its polarity from layer to layer, the order

parameter p_1 can be assumed to be positive in a half of layers (from 0 to 1), and the order parameter p_2 to be negative in another half of layers (from -1 to 0). Without the external electric field, the absolute values of polarization are equal in all layers; then by analogy with the recurrent relationship (14) we obtain:

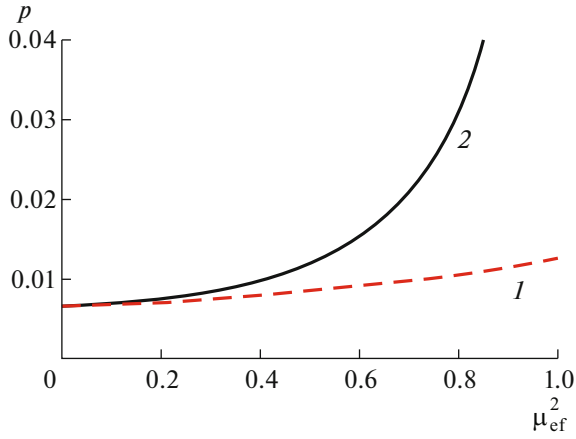


Fig. 4. The polar order parameter $p = P/(\rho\mu)$ as function of the square effective dipole moment $\mu_{ef}^2 = \mu/\sqrt{k_B T d^3}$ at $E = 0$, $\tilde{c}_p = c_p/(k_B T) = 4.74 \times 10^{-2}$ in (1) synclinic and (2) anticlinic smectics.

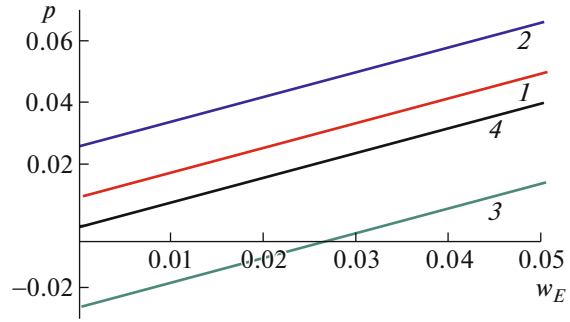


Fig. 5. The polar order parameter $p = P/(\rho\mu)$ as a function of the reduced energy of the electric field $w_E = E\mu/(k_B T)$ at $\theta = 15^\circ$, $\tilde{c}_p = 4.74 \times 10^{-2}$, $\mu_{ef}^2 = 0.77$, $d = h$ for (1) synclinic smectic LC, as well as for anticlinic smectic LC layers, where polarization and external electric field are (2) co-directed and (3) antidiagonal; (4) the average values in anticlinic smectic LC.

$$p = \frac{1}{I} \int_0^{2\pi} \cos \psi \exp \left\{ \left[\tilde{c}_p \sin \theta + \frac{1}{2} \mu_{ef}^2 \left(3 + \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi, \tag{15}$$

where $I = \int_0^{2\pi} \exp \left\{ \left[\tilde{c}_p \sin \theta + \frac{1}{2} \mu_{ef}^2 \left(3 + \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi.$

The polar order parameter as a function of the effective dipole moment, calculated from the recurrent relationships (14) and (15), is shown by curve 1 in Fig. 4 for the synclinic smectic and by curve 2 for the anticlinic smectic, respectively. In the first instance, it is worth mentioning that the polar order parameter is different of 0 (the short axes of the molecules have polar order) even without the transverse dipole in molecules (at $\mu_{ef} = 0$). This is due to the polar axis perpendicular to the plane of molecular inclination in smectic layers, which is characteristic of inclined smectics (at $\theta \neq 0$). In our simulated situation, the distance between the transverse dipoles of adjacent molecules, connected with their chiral centers and located near their flexible tails, is equal for molecules within a layer and in the neighboring layers ($h = d$). Therefore, the contribution to the average molecular field from the dipole–dipole interaction within each smectic layer exceeds the contribution made by the dipole–dipole interaction in the adjacent layers in absolute value and the presence of a molecule dipole thus increases the polar order parameter in both synclinic and anticlinic smectic phases (the higher the μ_{ef} magnitude is, the larger the p value of μ_{ef} is). However, since the interaction of dipoles becomes unfavorable in neighboring smectic synclinic layers (co-directional polarization vectors) and favorable in the anticlinic

phase (directional polarization vectors), the polar order parameter of each individual layer increases faster with the augmenting dipole moment. Here, the polarization averaged over all layers in anticlinic smectic is found to be zero, as it changes the polarity from layer to layer and remains equal in its absolute value in each layer.

4. THE EFFECT OF THE ELECTRIC FIELD ON THE POLARIZATION IN SYNCLINIC AND ANTICLINIC SMECTIC PHASES

Let a smectic liquid crystal be subjected to an electric field \mathbf{E} . To establish the polarization in a smectic, we will use Eqs. (1), (3), and (5). The electric field potential will be defined as

$$\Delta U_E(\psi) = -(\boldsymbol{\mu} \cdot \mathbf{E}) = -\mu E \cos \psi. \tag{16}$$

Integrating formulas (1), (3), (5), (14)–(16), we obtain the recurrent relationships that determine the polarization in synclinic and anticlinic smectics in the presence of the electric field and dipole–dipole interaction of molecules. For synclinic smectics we have:

$$p = \frac{1}{I} \int_0^{2\pi} \cos \psi \exp \left\{ \left[w_E + \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3 - \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi, \quad (17)$$

where
$$I = \int_0^{2\pi} \exp \left\{ \left[w_E + \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3 - \frac{d^3}{h^3} \right) p \right] \cos \psi \right\} d\psi.$$

where $w_E = E_\mu / (k_B T)$ is the effective reduced energy of the electric field. As was described in Section 3, in the anticlinic smectic beyond the electric field the polarization changes its polarity from layer to layer and it is equal in its absolute value in each layer. It was shown in [12–17] that like a synclinc smectic, an anticlinic smectic is oriented in the electric field so that the planes of inclination in all smectic layers are perpendicular to the direction of the electric field. Moreover,

in the anticlinic smectic the spontaneous polarization is found to be co-directed with the electric field in half of the layers (for these we introduce the polar order parameter p_1), whereas in the other half of the layers it is antidirectional (the polar order parameter p_2 was introduced for these layers). In the presence of the electric field the order parameters p_1 and p_2 are no more equal, even in their absolute values.

$$p_1 = \frac{1}{I_1} \int_0^{2\pi} \cos \psi \exp \left\{ \left[w_E + \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3p_1 - \frac{d^3}{h^3} p_2 \right) \right] \cos \psi \right\} d\psi, \quad (18)$$

where
$$I_1 = \int_0^{2\pi} \exp \left\{ \left[w_E + \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3p_1 - \frac{d^3}{h^3} p_2 \right) \right] \cos \psi \right\} d\psi,$$

$$p_2 = \frac{1}{I_2} \int_0^{2\pi} \cos \psi \exp \left\{ \left[w_E - \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3p_2 - \frac{d^3}{h^3} p_1 \right) \right] \cos \psi \right\} d\psi, \quad (19)$$

where
$$I_2 = \int_0^{2\pi} \exp \left\{ \left[w_E - \tilde{c}_p \sin \theta + \frac{1}{2} \mu_{\text{ef}}^2 \left(3p_2 - \frac{d^3}{h^3} p_1 \right) \right] \cos \psi \right\} d\psi.$$

The polar order parameter as a function of the effective energy of the interaction between a dipole and the electric field w_E is displayed in curve I in Fig. 5 for a synclinc smectic and by curves 2–4 for an anticlinic smectic.

Let us consider the anticlinic phase in detail. Knowing that the director direction alternates from layer to layer, remaining within the plane, we note that the spontaneous polarization changes its orientation to the opposite one from layer to layer, as well.

This means that in half of the layers the spontaneous polarization is co-directed with the field and the polarization has the same polarity at any electric field value. Curve 2 in Fig. 5 presents the order parameter p_1 in the layers where the polarization is co-directed with the electric field, while curve 3 in Fig. 5 denotes the order parameter p_2 in the layers where the polarization and the electric field are oriented oppositely. Curve 4 in Fig. 5 shows the average order parameter, which is equal to the average polarization over the entire bulk per molecule and referred to its dipole moment. As is obvious in curves 2 and 3 in Fig. 5, the order parameters p_1 and p_2 possess different polarities

and are equal in their moduli ($\langle p \rangle = 0$) in the lack of an electric field (at $w_E = 0$). The polarization in the anticlinic smectic increases with the electric field, but not as fast as in the synclinc smectic.

CONCLUSIONS

Expressions that describe the polarization in synclinc and anticlinic smectics as a result of the piezoelectric effect were obtained in the context of the molecular statistic approach. They also take the dipole–dipole interaction of molecules within a smectic layer and in the adjacent layers into consideration, as well as the influence of the electric field.

Since the piezoelectric constant and the effective dipole moment, which define the polarization, are molecular parameters (i.e., they can be evaluated for real molecules via quantum-chemistry methods), the correlation between the macroscopic state of a smectic and the parameters highlighting the structural features of its molecules were described in the present study.

In conclusion, the symmetry features of the individual molecules responsible for the formation of synclinc and anticlinic symmetry structures with certain

values of the polar order parameter (polarization) were elucidated, which is of great importance in the elaboration of various devices based on ferroelectric and antiferroelectric LCs, such as high-precision sensors.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (project no. 16-43-03010) and the Ministry of Science and Technologies of Taiwan (project no. 105WFA0951535).

REFERENCES

1. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, 1974).
2. S. Chandrasekhar, *Liquid Crystals* (Cambridge Univ. Press, 1977).
3. S. A. Pikin and V. L. Indenbom, *Ferroelectrics* **20**, 151 (1978).
4. V. L. Indenbom and S. A. Pikin, *Sov. Phys. Usp.* **21**, 487 (1978).
5. *Ferroelectric Liquid Crystals*, Ed. by J. W. Goodby (Gordon and Breach, New York, 1992).
6. I.-H. Lin, D. S. Miller, P. J. Bertics, et al., *Science* **332**, 1297 (2011).
7. Y. Chen, L. Lei, K. Zhang, et al., *Biomicrofluidics* **4**, 043002 (2010).
8. A. Fracois and M. Himmelhaus, *Appl. Phys. Lett.* **92**, 141107 (2008).
9. S. Soria, S. Berneschi, M. Bronci, et al., *Sensors* **11**, 785 (2011).
10. R. B. Meyer, *Mol. Cryst. Liq. Cryst.* **40**, 33 (1977).
11. R. B. Meyer, *Phys. Rev. Lett.* **22**, 918 (1969).
12. A. V. Emelyanenko, A. Fukuda, and J. K. Vij, *Phys. Rev. E* **74**, 011705 (2006).
13. A. V. Emelyanenko, *Phys. Rev. E* **82**, 031710 (2010).
14. A. V. Emelyanenko and M. A. Osipov, *Phys. Rev. E* **68**, 051703 (2003).
15. A. V. Emelyanenko, *Eur. Phys. J. E* **28**, 441 (2009).
16. A. V. Emelyanenko and K. Ishikawa, *Soft Matter* **9**, 3497 (2013).
17. A. V. Emelyanenko, *Ferroelectrics* **495**, 129 (2016).
18. W. Maier and A. Saupe, *Z. Naturforsch.* **14a**, 882 (1959).
19. W. Maier and A. Saupe, *Z. Naturforsch.* **15a**, 287 (1960).
20. M. A. Osipov and A. Fukuda, *Phys. Rev. E* **62**, 3724 (2000).

Translated by O. Maslova