

STATISTICAL, NONLINEAR,
AND SOFT MATTER PHYSICS

Local-Field Anisotropy of a Light Wave in Quasi-Two-Dimensional Soft-Matter Objects

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Abstract—Experimental values of the Lorentz tensor components L_j for uniaxial quasi-two dimensional “soft matter” objects on substrates (bilayer lipid membranes, multilayer Langmuir films, smectics A, hexatic smectics B, submicron films of discotics Col_{hd} , micron anisotropic films of liquid-crystal comblike polymers and macromolecular polymers, submicron films of conjugated conductive polymers), freely suspended submicron films of smectics A, and uniaxially stretched micron films of conjugated conductive polymers have been determined using dispersion of refractive indices in the visible range. The dependences of the components L_j on the type of orientation (axial, planar) of uniaxial molecules (structural units of the film) with respect to the optical axis of the film, the film thickness, the substrate type, the chemical structure of molecules, and their long-range orientational order are established. It is revealed that the smectic A–hexatic B phase transition and two-dimensional crystallization of the smectic layer lead to changes in the components L_j due to the change in the orientational ordering of molecules as a result of the relation between the orientational and hexatic order parameters. All the above objects are characterized by isotropization of the Lorentz tensor L and the local-field tensor f with a simultaneous decrease in the birefringence of the sample and in the anisotropy of the molecular polarizability due to the change in the electronic structure of molecules. The correction for the anisotropy of the local-field tensor f to the orientational order parameter or the anisotropy of the molecular polarizability increases. The existing model approaches to calculating the components L_j for the objects under consideration are compared with the experimental data.

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1. INTRODUCTION

The functioning of living systems and components of molecular electronics and optoelectronics are based on anisotropic molecular films with thicknesses varying from several nanometers to several microns. These are biomembranes [1, 2], Langmuir films [3, 4], smectics A with a liquid arrangement of molecules in layers, hexatic smectics B (hexatics) with a crystalline short-range order of molecules and a quasi-long-range orientational order of intermolecular bonds in layers, discotics $\text{Col}_{h(o,d)}$ with molecular columns forming a two-dimensional hexagonal lattice [5], and anisotropic films of comblike liquid-crystal polymers [6, 7], conventional macromolecular polymers [8–10], and conjugated conductive polymers [11–13].

The structure and molecular properties of these objects are most effectively investigated using linear [1–4, 6–14] and nonlinear optics [15, 16] and spectroscopic techniques [3, 17–21]. The interpretation of the optical properties of these uniaxial media is based on the relation of the measured components of the linear $\chi_j(\omega) = Nf_j(\omega)\gamma_j(\omega)$ and nonlinear

$$\chi_{i\dots l}(\omega_i, \dots, \omega_l) = Nf_i(\omega_i)\dots f_l(\omega_l)\gamma_{i\dots l}(\omega_i, \dots, \omega_l)$$

optical susceptibilities to the ensemble-averaged components of the molecular polarizability γ_j and hyper-

polarizabilities $\gamma_{i\dots l}$. Here, N is the number of molecules per unit volume. The components of the local-field tensor $f_j = 1 + L_j(\epsilon_j - 1)$ for light waves polarized along ($j = \parallel$) and normal ($j = \perp$) to the optical axis of the film \mathbf{n} relate the amplitude of the local field of the light wave $E_j^{\text{loc}}(\omega) = f_j(\omega)E_j(\omega)$ acting on a molecule to the amplitude of the macroscopic field of the light wave in the medium $E_j(\omega)$, where $\epsilon_j = n_j^2$, n_j are the refractive indices of the film and L_j are the Lorentz tensor components. An increase in the order of nonlinearity of the components $\chi_{i\dots l}$ leads to an increase in the role of the corrections for the local field, the inclusion of the dispersion of the components $f_j(\omega)$, and the anisotropy $\Delta f(\omega) = f_{\parallel} - f_{\perp}$. This requires information on the experimental values of the Lorentz tensor components L_j , which is one of the key problems in studying these objects.

The strength of the local dc or low-frequency ac electric field $E_{\parallel}^{\text{loc}}$ in Langmuir films [17, 19] or biomembranes [18] with a homeotropic (perpendicular to the film plane) molecular orientation can be determined using Stark spectroscopy with spectral probes: impurity dye molecules [17, 18] or a monolayer of dye molecules in a multilayer film [19]. How-

ever, the interpretation results of optical and nonlinear optical measurements does not require knowledge of the quantities $E_{\parallel}^{\text{loc}}$ and $E_j^{\text{loc}}(\omega)$.

Calculations of the components L_j and/or E_j^{loc} in membranes, Langmuir films, liquid crystals, and polymers have been performed within different approximations in a large number of works. Let us dwell on those dealing with the most characteristic approximations and comparison with experimental results. For lipid membranes [1, 22, 23] and Langmuir films [16, 24], the values of L_j and/or E_j^{loc} were calculated in terms of the continuum [1, 2] and lattice models of the medium with molecules in the form of point dipoles ($L_j^{(\text{pd})}$) [1, 16] or a set of point-polarizable subfragments ($L_j^{(\text{sps})}$) [22–24]. The analysis carried out in [1] has demonstrated that the values of $L_j^{(\text{pd})}$ and $L_j^{(\text{sps})}$ are inapplicable to the interpretation of the refractive indices of membranes simulated by a tetragonal lattice of hydrocarbon chains [22]. In particular, when a fatty acid molecule is chosen as a point-polarizable dipole with an axial ratio $a_{\parallel}/a_{\perp} \geq 6$ for the unit cell corresponding to the molecule, the overestimated value of $L_{\perp}^{(\text{pd})}$ leads to the inequality $\varepsilon_{\perp} < 0$ [1]. If the C_2H_4 group is chosen as an anisotropic point-polarizable chain subfragment [22] with an axial ratio of $a_{\parallel}/a_{\perp} \approx 0.5$ for the unit cell corresponding to the subfragment, the overestimated value of $L_{\parallel}^{(\text{sps})}$ leads to the inequality $\varepsilon_{\parallel} < 0$ [1]. In [22], a combination of the lattice and continuum models of a medium for the inclusion of the short-range and long-range dipole–dipole interactions between the C_2H_4 subfragments of hydrocarbon molecules in the monolayer membrane in the calculation of the quantities E_j^{loc} and n_j resulted in a negative value of $\Delta n = n_{\parallel} - n_{\perp}$, whereas the experimental value of this difference is positive [1]. A modified combination of the lattice and continuum models for the hexagonal packing of hydrocarbon chains with the CH_2 group as the anisotropic point-polarizable chain subfragment was used by Huang and Levitt [23] in calculating the components $L_j^{(\text{sps})}$ and the refractive indices n_j for monolayer membranes. The calculated components $L_j^{(\text{sps})}$ also lead to $\Delta n < 0$, whereas the experiments give $\Delta n > 0$ [1] and positive polarizability anisotropy $\Delta\alpha(\text{CH}_2) = \alpha_{\parallel} - \alpha_{\perp}$.

For lipid monolayer membranes, Den Engelsen [1] calculated the components L_j ($\text{Sp}L = 1$) in terms of the cylindrical Lorentz cavity model from the formula

$$L_{\perp} = \frac{l}{2(l^2 + D^2)^{1/2}}. \quad (1)$$

Here, l and D are the length and the diameter of the cylinder that contains the molecule whose axis is perpendicular to the layer surface. The agreement achieved in this case between the calculated values of n_j and the experimental results is explained by the appropriate choice of the quantities $\bar{\alpha}(\text{CH}_2) = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ and $\Delta\alpha(\text{CH}_2)$ under discussion [25], which lie outside the range of their known values according to the data obtained using independent optical and spectral methods [26]. Formula (1) was used by Salamon and Tollin [2] for bilayer membranes with an imperfect orientational order of molecules; in this case, instead of l and D , the authors used the projection of the molecule l' onto the normal to the membrane surface and $D' = (4a/\pi)^{1/2}$, where a is the membrane surface area per molecule. The results obtained in [1, 2, 23] will be discussed below.

In the calculations of the quantities $L_j^{(\text{sps})}$ and n_j [24] for model monolayer and multilayer Langmuir films with a close hexagonal packing of molecules in the layer, the molecule was simulated by a linear chain consisting of s isotropic point-polarizable beads with diameter D . For a monolayer with a homeotropic orientation of molecules, as the value of s increases, the component $L_{\parallel}^{(\text{sps})}$ rapidly tends to zero and, at $s \geq 7$, becomes negative and varies weakly. At $s = 5$, the values of $L_j^{(\text{sps})}$ [24] coincide with those calculated from formula (1) for $l = sD$. At $s \geq 5$, with an increase in the number of layers in the film, the components $L_j^{(\text{sps})}$ rapidly approach the limiting values $L_{\parallel}^{(\text{sps})} = 0$ and $L_{\perp}^{(\text{sps})} = 0.5$. In [24], the values of n_j for the monolayer film at $s = 5$ were calculated using the components $\gamma_{\parallel} = s\alpha$ and $\gamma_{\perp} = \alpha$ with the unreal value of α corresponding to the low refractive index $n_i = 1.22$ for the film in the isotropic phase. As a result, the refractive indices $n_{\parallel} = 1.421$ and $n_{\perp} = 1.105$ [24] appeared to be unrealistically low and the quantity Δn was multiply overestimated as compared to the experimental value [1, 3, 4].

In [27], the scheme of the calculations of the components L_j for smectics A and B uses the incorrect expression [28, 29] for the average molecular polarizability $\bar{\gamma}$, which leads to the inequality $\Delta f > 0$ [30] and contradicts the experimental results [31].

The components L_j for anisotropic amorphous and crystalline polymers were calculated in terms of the continuum [32–34] and lattice models of the medium [26, 35]. The continuum models involved the spherical ($L_j = 1/3$ [32]), cylindrical (expression (1) [33]), and ellipsoidal [34] Lorentz cavity models for a “polarizable segment” of the polymer chain; however, the choice of this segment is ambiguous. This circumstance is responsible for the uncertainty in the anisotropy of the cavity corresponding to the polarizable segment and the values of L_j [33, 34]. The microscopic

calculations of the components L_j were performed within the lattice models in which the polymer molecule was simulated by a chain of anisotropically polarizable segments [26] or a uniformly polarizable rod [35]. In view of the ambiguity of the choice of these segments for a number of polymers with $\Delta n > 0$, the calculated components L_j resulted in negative values of the polarizability anisotropy of the segment $\Delta\alpha$ [26, 34], which contradicts positive values of $\Delta\alpha$ according to the data of independent optical measurements [26]. The inadequacy of the methods for calculating the components L_j for anisotropic polymer films and the absence of experimental values of these quantities led to wide use of the spherical Lorentz cavity model [10, 32, 36, 37] for quantitative interpretation of the results of optical and spectral measurements.

Model (1) with the limiting values $L_{\parallel} = 0$ and $L_{\perp} = 0.5$ has been used in the theory of electronic and optical properties of conjugated conductive polymers [38, 39]. Although the inclusion of a real anisotropy of the tensors L and f is necessary for interpreting the optical and spectral properties of conjugated polymers [13], information on the experimental values of L_j and f_j for these objects is lacking.

In this paper, a method is proposed for the experimental determination of the components L_j for uniaxial molecular films with the use of the dispersion of the refractive indices $n_j(\lambda)$ in the visible range. Earlier, this approach was developed for optically positive calamitic liquid crystals consisting of rodlike molecules, and it was tested and confirmed for nematic liquid crystals of different chemical classes [40] with the known values of L_j according to independent spectral measurements [41]; as well, it was used for cholesteric liquid crystals [42]. In the present work, the proposed method is generalized to optically negative media (including discotic liquid crystals with disk-shaped molecules) and uniaxial polymer films, which can be optically positive and negative depending on the preparation technique. The essence of the proposed method for low-molecular and polymer optically positive and negative media is described in Section 2. In Section 3, we investigate quasi-two-dimensional objects of different types and a separate subsection is devoted to each type of objects. The established general regularities inherent in all objects are discussed in Section 4. The main results of the work and conclusions are summarized in Section 5.

2. DISPERSION OF THE REFRACTIVE INDICES $n_j(\lambda)$ AND COMPONENTS L_j

Let us discuss the influence of a substrate on the effective dimension of the objects under investigation and the determined components L_j . The "softness" of these objects is associated with the weakness of anisotropic intermolecular interactions responsible for the orientational order of molecules and the optical

anisotropy of the medium [5]. The thickness h of the film corresponding to its quasi-two-dimensional character is determined by the film characteristic under investigation [43]. Here, the components L_j are determined from the refractive indices $n_j(\lambda)$, which depend on the orientational order of molecules and change along with it due to the interaction of the film with the substrate. In this case, the anisotropic molecular film on the substrate can be assigned to quasi-two-dimensional systems at $h < h_0$, where h_0 is the limiting thickness at which the substrate substantially affects the orientational order of molecules with respect to optical axis \mathbf{n} of the film and the orientation of the \mathbf{n} axis in the film [43]. The thickness h_0 depends on the nature and structure of the film, the orientation of the \mathbf{n} axis at the boundary with the substrate, the film surface topology, the nature of the interaction forces with the substrate, and other factors [43]. A specific feature of anisotropic soft matter objects is that, for them, the thickness h_0 is several orders of magnitude larger than the molecular thickness $h_m \approx 5 \times 10^{-4} \mu\text{m}$ [43, 44]. This quantity is $h_0 \approx 0.5\text{--}1.0 \mu\text{m}$ [43] for thermotropic nematics and cholesterics, $h_0 \gg 1 \mu\text{m}$ [5, 43] for smectics A and B (biomembranes, Langmuir films) with a homeotropic orientation of molecules, and $h_0 \approx 10\text{--}20 \mu\text{m}$ for anisotropic polymer films [10]. The films investigated here (especially layered systems, such as biomembranes, Langmuir films, and smectics) satisfy the condition $h \ll h_0$ and are quasi-two dimensional objects. Since the refractive indices $n_j(\lambda)$ for these films are highly sensitive to the change in the substrate [4, 43], the determination of the components L_j from the experimental dependences $n_j(\lambda)$ makes it possible to reveal the influence of the substrate on the values of L_j .

Another aspect of the quasi-two-dimensionality concerns smectics B (hexatics). In these objects, the long-range orientational order of long molecular axes with respect to the normal to the smectic layer combines with the quasi-long-range orientational (hexatic) order of intermolecular bonds in the layer. The smectic A–smectic B (SmA–SmB) phase transition is accompanied by a change in the refractive indices n_j and the dependences $n_j(\lambda)$ [45]. This makes it possible to determine the change in the components δL_j due to the hexatic ordering of molecules in the layer upon the SmA–SmB transition and to establish the relation of the quantity δL_j to the change in the orientational order of molecules upon this transition [5].

For discotic liquid crystals, the size effects were discussed in detail in [44, 46]. In the case of the quasi-two-dimensional films of discotic liquid crystals Col_{hd} [14] under investigation with the column orientation parallel to the substrate and $h \ll h_0$, the presence of the substrate suppresses fluctuations of synchronous bending of columns [5, 44, 46] that affect the measured values of n_j . This minimizes the influence of fluctuation effects on the determined components L_j .

The transverse oscillations of a freely suspended smectic film make it impossible to assign it to a true

two-dimensional system even in the case where the film thickness is on the order of one to two monolayers [47]. These oscillations with anomalously weak damping are responsible for the strong fluctuation effects in the dynamics of the film [47]. For the multilayer smectic A films under consideration, the situation is intermediate between a monomolecular film [47] and a bulk sample [5], so that fluctuation effects and an undulation mode of the splay-deformation of smectic layers in the film with unaffected interlayer spacing should occur [5]. Both factors affect the measured values of the refractive indices n_j , because they lead to a mean-square deviation $\langle \sin^2 \delta \rangle_n$ of the local normal $\mathbf{n}(\mathbf{r})$ to the film from the average normal \mathbf{n}_0 (optical axis). In order to empirically assign the smectic film to quasi-two-dimensional objects, the value of h_0 can be estimated from the dependence $n_j(h)$ [48].

Now, we turn to the determination of the components L_j from the dependences $n_j(\lambda)$. Let us consider a uniaxial molecular film in which the optical axis \mathbf{n} (director) is parallel to the film plane (planar orientation) or perpendicular to the film plane (homeotropic orientation). We assume that the film consists of uniaxial structural units with the axial symmetry axis \mathbf{l} . The polarizability tensor γ of the structural unit is determined by the mean value of $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and the anisotropy $\Delta\gamma = \gamma_l - \gamma_t$, where $\gamma_{l,t}$ are the longitudinal and transverse components of the quantity γ . The degree of orientational ordering of structural units with respect to the \mathbf{n} axis is characterized by the order parameter $S = \langle 3 \cos^2 \theta_m - 1 \rangle / 2$ [5], where θ_m is the angle between the \mathbf{l} and \mathbf{n} axes and the angle brackets $\langle \dots \rangle$ indicate the averaging over an ensemble. The sign of the order parameter S determines the type of orientation of structural units, i.e., the axial orientation ($0 < S \leq 1$) or the planar orientation ($-0.5 \leq S < 0$). The procedure for determining the components L_j depends on the optical sign of the film (sign of the quantity Δn), which coincides with the sign of the parameter $q = \Delta\gamma S / 3\bar{\gamma}$ [30] and is determined by the type of the orientation of structural units and the polarizability anisotropy $\Delta\gamma$. For freely suspended smectic A films, the parameter q involves the product $S(1 - 3 \langle \sin^2 \delta \rangle_n / 2)$ instead of the parameter S [31].

Among the objects under investigation, biomembranes [1, 2], Langmuir films [3, 4], smectics A and B [45], freely suspended films of smectics A [48], comb-like nematic liquid-crystal polymers with rodlike side fragments (oriented in the electric field) [6], uniaxial films of conjugated polymers on orienting substrates [11], and uniaxially stretched films of conventional and conjugated polymers [12, 13, 21] belong to optically positive media with Δn , $\Delta\gamma$, $S > 0$, and axial orientation of structural units.

The optically negative media (discussed below) with Δn and $q < 0$ involve objects with axial (discotics

$\text{Col}_{h(o,d)}$) and planar orientations of structural units. The planar orientation occurs for films of conventional [8–10] and conjugated polymers [11, 20, 49], films of comblike liquid-crystal polymers [7], which are prepared by leveling a gel polymer solution over the substrate surface with a special blade (the doctor blading technique) [8, 9, 49] or by centrifugal spreading of a polymer solution droplet over the surface of a spinning substrate (the spin-coating technique) [7, 11, 20], and amorphous polymer films produced by stretching in two mutually perpendicular directions in the film plane [21]. We now consider the procedures for determining the components L_j for low-molecular media with different signs, as well as for conventional and conjugated macromolecular polymers.

2.1. Optically Positive Media

For optically positive media, in which molecules with $\Delta\gamma > 0$ are structural units, the inequality $\varepsilon_{\parallel} > \varepsilon_{\perp}$ holds true. In the optical transparency range, we introduce the parameters

$$\bar{\varepsilon} = \frac{\varepsilon_{\parallel} + 2\varepsilon_{\perp}}{3}, \quad Q = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\bar{\varepsilon} - 1}$$

and the quantities

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad (2)$$

$$b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0,$$

$$b_1 = \frac{2r_0Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1 \left(\frac{6 + Q}{Q} \right)^2.$$

With allowance made for the condition $\text{Sp}L = 1$, it is sufficient to determine the component L_{\perp} related to the above quantities by the expression [30]

$$L_{\perp} = L_{\perp k} - \frac{\bar{\varepsilon} + 2}{12(\bar{\varepsilon} - 1)} \quad (3)$$

$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}],$$

where

$$L_{\perp k} = \frac{3 + 2Q}{3(3 + Q)}.$$

This expression includes the function $b(\lambda, T)$ dependent on the unknown quantity $\bar{\gamma}$. For liquid crystals with the values of $L_{\perp}(T)$ and $n_j(\lambda, T)$ known from experiments [41], the function $b(\lambda, T)$ obtained from formula (3) for a fixed value of $L_{\perp}(T)$ in the visible range varies only slightly and is well approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \dots + a_m(T)\lambda^m \quad (4)$$

with a degree of $m \leq 2$ [40]. Correspondingly, the proposed method for determining the component $L_{\perp}(T)$ at a fixed temperature of a liquid crystal is as follows. At the known refractive indices $n_j(\lambda, T)$ for a discrete

set of wavelengths λ_i ($i = 1-p$) in the visible spectral range, the function $b(\lambda, T)$ in the range $\lambda_1 - \lambda_p$ is approximated by polynomial (4). The structural characteristic of the film $L_{\perp}(T)$ does not depend on λ , and to each temperature there correspond $m + 2$ unknown quantities ($L_{\perp}^{(m)}, a_0 - a_m$). They are found from the system of $m + 2 = p$ equations (3), each of which corresponds to one of the wavelengths λ_i . Therefore, the degree m of polynomial (4) and the maximum degree of approximation for the component $L_{\perp}^{(m)}(T)$ are determined by the number p of wavelengths λ_i . The use of a higher approximation in polynomial (4) suggests a higher accuracy of the refractive indices $n_j(\lambda, T)$; otherwise, the system of equations for the quantities ($L_{\perp}^{(m)}, a_0 - a_m$) can have no physical solutions or lead to an irregular dependence $L_{\perp}^{(m)}(T)$. For nematic liquid crystals of different chemical classes with the components $L_{\perp}(T)$ known from spectral measurements [31, 41], the use of this procedure leads to components $L_{\perp}^{(m)}(T)$ that coincide with the values of $L_{\perp}(T)$ but are considerably more accurate [40].

Now, we demonstrate the importance of experimental values of L_j for liquid crystals with large and small birefringences Δn , because there is the widespread opinion in the literature that the anisotropy of the tensors L and f can be ignored in the quantitative interpretation of refractometric data for objects with small values of Δn (biomembranes, Langmuir films, anisotropic polymer films). The parameter q determined from the refractometric data in the presence of the components L_j can be represented in the form [30]

$$q = q_0(1 + \sigma), \quad (5)$$

where $q_0 = q(\Delta f = 0) = Q/3$ and the correction σ for the anisotropy Δf is given by the expression

$$\sigma = -\frac{\Delta f(3 + 2Q)(9 - Q^2)}{Q[3(3 + Q)(\bar{\epsilon} + 2)r_0 + \Delta f(3 - Q)(3 + 2Q)]}. \quad (6)$$

The sign of the correction σ is opposite to the sign of the anisotropy Δf . In view of the proportionality $\sigma \propto \Delta f/Q$ in the limit of small values of Δn for objects with $\Delta \gamma$ and $Q \rightarrow 0$, the correction σ is determined not by the quantity Q but by the limiting value $(\Delta f/Q)_{\text{lim}} = (\Delta f/Q)_{Q \rightarrow 0}$. The anisotropy Δf can be written in the form

$$\Delta f = \frac{Q(\bar{\epsilon} - 1)(1 - A)}{3}, \quad A = \frac{L_{\perp} - 1/3}{L_{\perp k} - 1/3}. \quad (7)$$

For calamitic liquid crystals in the visible spectral range, the relationships $L_{\perp} > L_{\perp k} > 1/3$, $A > 1$, $\Delta f < 0$, and $\sigma > 0$ are valid [31, 40–42]. With due regard for the smallness of $Q \ll 3$ in the visible range for calamitic liquid crystals [31], it follows from expressions (6) and (7) that, for a particular liquid crystal, the correction σ depends weakly on the temperature of the mesophase

with a variation in the quantities S and Q . However, at a fixed quantity S and with a change in the chemical and electronic structure of molecules, the values of Δn and $Q \propto \Delta n$ can change by several orders of magnitude due to the change in the quantity $\Delta \gamma$. In this case, at $\Delta \gamma$ and $Q \rightarrow 0$, we have q and $\Delta f \rightarrow 0$; however, at $A \rightarrow A_{\text{lim}}$, the correction σ tends to the limit

$$\sigma_{\text{lim}} = \frac{(A_{\text{lim}} - 1)(\bar{\epsilon} - 1)}{\bar{\epsilon} + 2}. \quad (8)$$

With allowance made for expressions (6) and (7), at $A_{\text{lim}} \approx A$, we have $\sigma > \sigma_{\text{lim}}$. For biomembranes [1, 2], Langmuir films [4], and anisotropic polymer films [31] for the same small values of Δn and Q as for cholesteric liquid crystals [42], we can expect small values of Δf but large values of $\sigma \geq \sigma_{\text{lim}}$. For typical values of $A_{\text{lim}} \approx A > 2$ and $\bar{\epsilon} \approx 2.5$, as for cholesteric liquid crystals in the visible range [42], from expression (8), we obtain $\sigma_{\text{lim}} > 1/3$; i.e., the correction to the quantity q_0 is significant despite a small value of Δf (formula (7)).

The model with the component $L_j = 1/3$ usually used for uniaxial polymer films with a small value of Δn [10, 32, 36, 37] corresponds to the values of $A = A_{\text{lim}} = 0$ and $\Delta f = Q(\bar{\epsilon} - 1)/3$. They lead to large negative values of σ and $\sigma_{\text{lim}} = -(\bar{\epsilon} - 1)/(\bar{\epsilon} + 2)$, which contradict experimental data obtained using spectral methods [31].

2.2. Optically Negative Media

The columnar discotic liquid crystals $\text{Col}_{h(o,d)}$ with $S > 0$ and $\Delta \gamma < 0$ are typical examples of optically negative media. Disk-shaped molecules of these liquid crystals are located in columns with short-range (Col_{hd}) or quasi-long-range (Col_{ho}) positional order. The axes of molecules are perpendicular to molecular cores and oriented along the columns, which are parallel to the optical axis \mathbf{n} of the film. In the plane perpendicular of the \mathbf{n} axis, the columns form a hexagonal lattice [5]. For these liquid crystals with $\epsilon_{\parallel} < \epsilon_{\perp}$, we use the parameters $q_d = -q$ and $Q_d = -Q$ and the quantities

$$\begin{aligned} r_{0d} &= 1 - \frac{2Q_d^2(\bar{\epsilon} - 1)}{3(3 - Q_d)(\bar{\epsilon} + 2)}, \\ d &= \frac{3(\bar{\epsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\epsilon} + 2)} - r_{0d}, \\ d_1 &= \frac{2r_{0d}Q_d^2}{(3 + Q_d)(3 - 2Q_d)}, \\ d_2 &= d_1 \left(\frac{6 - Q_d}{Q_d} \right)^2. \end{aligned} \quad (9)$$

These quantities and the tensor component L_{\perp} are related by the expression [30]

$$L_{\perp} = L_{\perp k} + \frac{\bar{\epsilon} + 2}{12(\bar{\epsilon} - 1)} \quad (10)$$

$$\times [(d_1 d_2)^{1/2} + d - [(d_1 - d)(d_2 - d)]^{1/2}],$$

where

$$L_{\perp k} = \frac{3 - 2Q_d}{3(3 - Q_d)}.$$

The function $d(\lambda, T)$ is approximated by polynomial (4). The quantities $(L_{\perp}^{(m)}, a_0 - a_m)$ are determined according to a procedure similar to that described above from the known refractive indices $n_j(\lambda, T)$ for the set of wavelengths λ_i ($i = 1 - p$) from system of equations (10), each of which corresponds to one of the wavelengths λ_i . For discotic liquid crystals, we have

$$q_d = q_{0d}(1 + \sigma_d), \quad (11)$$

where $q_{0d} = Q_d/3$ and the correction σ_d has the form

$$\sigma_d = \frac{\Delta f_d(3 - 2Q_d)(9 - Q_d^2)}{Q_d[3(3 - Q_d)(\bar{\epsilon} + 2)r_{0d} + \Delta f_d(3 + Q_d)(3 - 2Q_d)]}. \quad (12)$$

The sign of the correction σ_d coincides with the sign of the anisotropy

$$\Delta f_d = \frac{Q_d(\bar{\epsilon} - 1)(A - 1)}{3}. \quad (13)$$

For discotic liquid crystals in the optical transparency range, the inequalities $L_{\perp} < L_{\perp k} < 1/3$, $A > 1$, and $\Delta f_d > 0$ and $\sigma_d > 0$ are valid [30, 31, 50]. The changes $\Delta \gamma_d$ and $Q_d \rightarrow 0$ due to the change in the chemical and electronic structure of disk-shaped molecules result in tendencies q_d and $\Delta f_d \rightarrow 0$, whereas the quantity σ_d tends to limit (8). However, in this case, with allowance made for expressions (12) and (13) at $A_{\text{lim}} \approx A$, we have $\sigma_d < \sigma_{\text{lim}}$.

2.3. Polymer Films

These media differ from low-molecular media only in the sense of quantities that are involved in the parameter q . For calamitic comblike liquid-crystal polymers, rodlike side mesogenic fragments make the dominant contribution to the birefringence of films and are characterized by the polarizability anisotropy $\Delta \gamma_F \gg \Delta \gamma_m$. Here, $\Delta \gamma_m$ is the polarizability anisotropy of the monomer unit of the main chain to which the side fragment is bonded. Therefore, we can naturally identify the structural unit of calamitic liquid-crystal polymers with the side fragment together with the monomer unit of the main chain to which the side fragment is bonded. The \mathbf{l} axis of this structural unit is parallel to the longitudinal axis of the rigid aromatic core of the side fragment, and the polarizability anisotropy $\Delta \gamma \approx (\Delta \gamma_F - \Delta \gamma_m/2) > 0$ is included in the parameter q .

For flexible-chain polymer molecules, the \mathbf{l} axis coincides with the direction of the vector \mathbf{h} between the ends of the chain and the polarizability anisotropy of the macromolecule is $\Delta \gamma = (M/M_m)\Delta \alpha_m S_m$ [51]. Here, M and M_m are the molecular weights of the macromolecule and its monomer unit, respectively; $\Delta \alpha_m$ is the polarizability anisotropy of the uniaxial monomer unit; $S_m = (3 \cos^2 \vartheta_m - 1)/2$; ϑ_m is the angle between the longitudinal axis \mathbf{l}_m of the monomer unit and the \mathbf{l} axis; and the overbar indicates averaging over the orientations of monomer units with respect to the \mathbf{l} axis. The quantity S_m is the intramolecular orientational order parameter of monomer units with respect to the \mathbf{l} axis [51]. Rigid-chain molecules of conjugated polymers consist of linear conformational subunits of different types i [52], which differ in the number of constituent monomer units and the values of $\Delta \alpha_i$ and S_i . The polarizability anisotropy of this molecule is $\Delta \gamma = N \sum_i x_i \Delta \alpha_i S_i$, where $x_i = N_i/N$ is the fraction of subunits of the i th type in the number of subunits N in the molecule. For flexible-chain and rigid-chain polymer molecules, we have $\Delta \gamma > 0$.

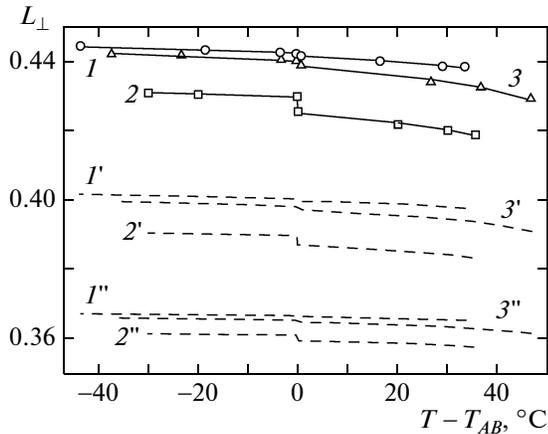
For optically positive films of calamitic comblike liquid-crystal polymers (flexible-chain and rigid-chain conjugated polymers) with the axial orientation of side mesogenic fragments (macromolecular axes $\mathbf{l} \parallel \mathbf{h}$), expressions (2)–(8) hold true. For optically negative films of liquid-crystal polymers (flexible-chain and rigid-chain polymers) with the planar orientation of side fragments (macromolecular axes $\mathbf{l} \perp \mathbf{h}$), it is necessary to use quantities $q_d = -q$ and $Q_d = -Q$ and formulas (9)–(13).

3. OBJECTS OF INVESTIGATION AND RESULTS

Now, we apply the described approach to determining the components L_{\perp} for molecular films of different natures with the known refractive indices $n_j(\lambda, T)$ and check the consequences of relationships (6)–(8), (12), and (13). Unlike a number of cited works in which the index \perp (\perp) means that the direction of the electric vector \mathbf{E} of the light wave is parallel (perpendicular) to the film plane, which is equivalent only to the homeotropic orientation of the director \mathbf{n} , here, this index corresponds to the polarization $\mathbf{E} \parallel \mathbf{n}$ ($\mathbf{E} \perp \mathbf{n}$) for the planar and homeotropic orientations of the director \mathbf{n} .

3.1. Optically Positive Media

3.1.1. The bilayer lipid membrane POPC x (1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine with an impurity of chromophore-labeled phosphatidylcholine molecules at a concentration equal to $x\%$) with the thickness $h = 5.2$ nm and the homeotropic orientation of the director \mathbf{n} on the SiO₂ substrate [2].



Temperature dependences of the quantities (I-3) $\langle L_{\perp}^{(0)} \rangle$ (points), (I'-3') $L_{\perp k}$, and (I''-3'') $L_{\perp}^{(H)}$ at $\lambda = 0.5893 \mu\text{m}$ for the liquid crystals (I, I', I'') B2.2, (2, 2', 2'') B8.5, and (3, 3', 3'') BPh.4. Solid lines I-3 correspond to relationship (14) for the quantities $L_{\perp} = \langle L_{\perp}^{(0)} \rangle$ at $\lambda = 0.5893 \mu\text{m}$.

In order to avoid cumbersome structural chemical formulas of molecules of the compounds under consideration, herein, we will present their chemical names or abbreviations used by the authors of the cited works.

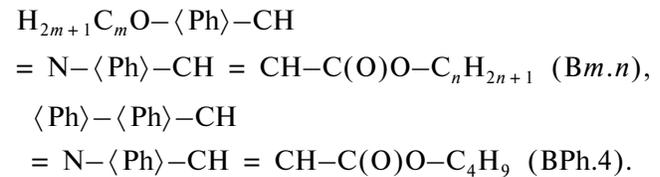
The refractive indices $n_j(\lambda)$ measured for the membranes POPCx at $\lambda_1 = 0.5435 \mu\text{m}$ and $\lambda_2 = 0.6328 \mu\text{m}$ [2] lead to the components $L_{\perp}^{(0)} = 0.374$ (POPC4) and 0.363 (POPC10), thus indicating that the components L_j are highly sensitive to the concentration of impurity molecules. At $\lambda = \lambda_2$ for the membrane POPC4 (POPC10) at the small value of $\Delta f/\bar{f} = -0.072$ (-0.041), we have the large correction $\sigma = 0.565$ (0.313) close to $\sigma_{\text{lim}} = 0.529$ (0.296) at $A_{\text{lim}} = A = 2.834$ (2.008). For the close components $L_{\perp}^{(0)}$, the corrections σ for the membranes POPC4 and POPC10 differ substantially.

3.1.2. Langmuir films Cd-A (cadmium arachidate) with a number of layers from 29 to 41 and a thickness of 77.7–109.9 nm on the glass or PMMA (polymethylmethacrylate) substrates.

For these films, the refractive indices $n_j(\lambda)$ at $\lambda_1 = 0.4579 \mu\text{m}$, $\lambda_2 = 0.5145 \mu\text{m}$, and $\lambda_3 = 0.6328 \mu\text{m}$ are given in [4]. From these data for the Cd-A films on the glass substrates, we obtain the component $L_{\perp}^{(1)} = 0.365$ and the value of $\langle L_{\perp}^{(0)} \rangle = 0.362 \pm 0.003$ averaged over three components $L_{\perp}^{(0)}$ corresponding to combinations of two values of the wavelength λ_i from the set λ_{1-3} . For the Cd-A films on the PMMA substrates, we have $L_{\perp}^{(1)} = 0.356$ and $\langle L_{\perp}^{(0)} \rangle = 0.352 \pm 0.002$. For

each substrate, the values of $L_{\perp}^{(1)}$ and $\langle L_{\perp}^{(0)} \rangle$ are in agreement and the accuracy of the parameters $\langle L_{\perp}^{(0)} \rangle$ suggests that the components L_{\perp} are determined with a high accuracy, despite a low accuracy of ± 0.01 for the refractive indices $n_j(\lambda)$ [4]. The dependence of the component L_{\perp} on the substrate type is weak due to the large number of layers but is reliably revealed by the method used. At $\lambda = \lambda_3$ and $L_{\perp} = L_{\perp}^{(1)}$, for the Cd-A films on the glass (PMMA) substrates, to a small value of $\Delta f/\bar{f} = -0.064$ (-0.041) there corresponds a large value of $\sigma = 0.739$ (0.563) close to $\sigma_{\text{lim}} = 0.703$ (0.542) at $A_{\text{lim}} = A = 3.247$ (2.759). At a small difference between the components $L_{\perp}^{(1)}$, the values of σ for the Cd-A films on different substrates differ significantly. With a decrease in the wavelength λ , in view of the normal dispersion of the quantities $n_j(\lambda)$ and $\Delta n(\lambda)$, the correction $\sigma(\lambda)$ decreases and we have $\sigma = 0.252$ (0.384) at $\lambda = \lambda_1$ for the Cd-A films on the glass (PMMA) substrates.

3.1.3. In this work, the change in the component $L_{\perp}(T)$ upon the SmA–SmB transition is investigated for the following liquid crystals B2.2, B8.5, and BPh.4:



Here and below, $\langle \text{Ph} \rangle$ is the phenyl ring. The refractive indices $n_j(\lambda, T) \pm 0.0005$ for the smectic A and B phases of these liquid crystals were measured on a refractometer and tabulated in [45] at the wavelengths $\lambda_1 = 0.5461 \mu\text{m}$, $\lambda_2 = 0.5893 \mu\text{m}$, and $\lambda_3 = 0.6438 \mu\text{m}$. Under conditions of total internal reflection for a light wave at the glass–liquid crystal boundary, the depth of its penetration into the liquid-crystal layer is of the order of λ and equal to the effective thickness h of the liquid-crystal layer to which the determined refractive indices $n_j(\lambda, T)$ correspond. Since the relationship $\lambda_i \approx h \ll h_0$ [43] is valid for the above wavelengths λ_i , the refractive indices $n_j(\lambda, T)$ [45] correspond to submicron quasi-two-dimensional samples of smectics A and B.

The figure shows the dependences of the quantity $\langle L_{\perp}^{(0)}(T) \rangle$ on $\Delta T = T - T_{AB}$, where T_{AB} is the temperature of the SmA–SmB transition. As a result of the narrow spectral range λ_{1-3} , the scatter of the values of $L_{\perp}^{(0)}(T)$ is smaller than that of the values of $L_{\perp}^{(1)}(T)$. For all liquid crystals, the deviation of the quantity $L_{\perp}^{(0)}(T)$ from $\langle L_{\perp}^{(0)}(T) \rangle$ at each temperature does not exceed 0.001. For the discussed liquid crystals with a long chain of π -electron conjugation of molecular

fragments and large values of $\Delta\gamma$ and Δn , the quantities $L_{\perp} = 0.42\text{--}0.44$ for the smectic phases are larger than $L_{\perp} = 0.40\text{--}0.41$ (0.365) for smectic A phases of cyanobiphenyls [40, 41] (cholesteric liquid crystals [42]) with moderate (small) values of $\Delta\gamma$ and Δn . According to the X-ray diffraction data [53], in the smectic B phase in the vicinity of the temperature T_{AB} , the changeover from the compound B2.2 to the compound B8.5 with an increase in the length of terminal alkyl chains of the molecule is accompanied by an increase in the interlayer distance d_{\parallel} from 21.4 to 31.6 Å without change in the intermolecular distance $d_{\perp} = 4.1$ Å in the layer. However, this leads to a decrease in the component L_{\perp} , which indicates that the continuum model (1) is inapplicable. From this model, with due regard for $l = d_{\parallel}$ and $D = d_{\perp}$, we obtain the component $L_{\perp} = 0.491$ (0.496) for the liquid crystal B2.2 (B8.5), which differs substantially from the experimental data.

In the series of compounds B8.5, BPh.4, and B2.2, an increase in the component L_{\perp} upon the SmA–SmB transition corresponds to a change in the character of this transition from a pronounced first-order transition for the compound B8.5 to a weak first-order transition for the other liquid crystals. A small change in the component L_{\perp} and a very weak increase in the component $L_{\perp}(T)$ with a decrease in temperature correspond to a weak stepwise increase in the parameter d_{\parallel} for the compound B2.2 at the point T_{AB} [53]. For three liquid crystals in both smectic phases at a fixed ΔT , the ratio between the quantities L_{\perp} is similar to the ratio between the quantities $L_{\perp k}$. This suggests the relation

$$L_{\perp}(\Delta T) = A(\lambda)L_{\perp k}(\Delta T, \lambda) + B(\lambda), \quad (14)$$

which is invariant with respect to the SmA–SmB transition. For the liquid crystals under consideration, the dependences constructed using relationship (14) (shown by the solid lines in the figure) approximate the experimental dependences $L_{\perp}(\Delta T) = \langle L_{\perp}^{(0)}(\Delta T) \rangle$ with the correlation coefficient $R \geq 0.993$. The coefficients in formula (14) are related by the expression $B = (1 - A)/3$ with a high accuracy. In particular, at $\lambda = 0.5893$ μm, we have $B = -0.194$ (–0.237) and $(1 - A)/3 = -0.196$ (–0.236) for the compound B2.2 (B8.5). This means that the coefficient A in formula (14) has the same meaning as in relationship (7); in this case, the relationship $A = \text{const}$ holds true, which

was previously predicted for nematic liquid crystals [31], was recently confirmed for cholesteric liquid crystals and is invariant with respect to the cholesteric–SmA transition [42].

As a result of the inequality $Q \ll 3$, the relationship $(L_{\perp k} - 1/3) \propto Q \propto S$ (5) is valid. Therefore, it follows from the condition $A = \text{const}$ that the change in the component $L_{\perp}(T)$ in uniaxial liquid crystals and upon transitions between uniaxial phases is associated with orientational ordering of molecules. In the case of the smectic liquid crystals under consideration, the change in the component $L_{\perp}(T)$ upon the SmA–SmB transition and in the hexatic B phase is caused by the change in the order parameter S due to the relation between the hexatic and orientational orderings of molecules [5].

In the hexatic B phase at $T \approx T_{AB}$ and $\lambda_3 = 0.6438$ μm, the liquid crystals under investigation are characterized by $\Delta n = 0.350$ for the B2.2 compound, 0.265 for the B8.5 compound, and 0.345 for the BPh.4 compound [23]. The components L_{\perp} presented in the figure and the refractive indices $n_j(\lambda_3)$ [45] give $\sigma = 0.287$ for the B2.2 compound, 0.304 for the B8.5 compound, and 0.309 for the BPh.4 compound. For $Bm.n$ molecules, a change in the correction σ with an increase in the length of terminal alkyl chains is opposite to a change in the quantities L_{\perp} and Δn .

The inequalities $L_{\perp} > L_{\perp k}$, $b < 0$, and $\Delta f < 0$ are true for the compounds under consideration. In the model for the calculation of the component L_{\perp} for smectics A and B [27], the authors used the expression [28, 29]

$$\bar{\gamma} = \frac{3(\bar{\epsilon} - 1)}{4\pi N(\bar{\epsilon} + 2)}. \quad (15)$$

It can be seen from formula (2) that this expression corresponds to the quantity $b = 1 - r_0 = b_H > 0$ and the relationship $L_{\perp}^{(H)} < L_{\perp k}$, which follows from formula (3) and is independent of the chemical nature of molecules and the birefringence Δn . The values of $L_{\perp}^{(H)}$ in the figure and the corresponding values of $\Delta f_H > 0$ and $\sigma_H < 0$ contradict experimental data. It should be noted that the dependences $L_{\perp}^{(H)}(\Delta T)$ are approximated by expression (14) with the correlation coefficient $R \geq 0.9993$.

3.1.4. Freely suspended films of the compound



in the smectic A phase at a temperature of 145°C [48]. For these films with the homeotropic orientation of the director \mathbf{n} and $h = 168.88\text{--}1191.40$ nm, the graphic dependences $n_j(\lambda)$ in the range $\lambda = 0.4\text{--}1.0$ μm are presented in [48]. For $h \geq 270$ nm, the dependences $n_j(\lambda)$ almost coincide with those for bulk samples,

whereas the refractive indices $n_j(\lambda)$ at $h = 168.88$ nm noticeably differ [48]. This corresponds to a value of $h \approx 270$ nm. In this work, the components L_{\perp} were determined for the MHPOBC films with $h = 168.88, 260.73,$ and 266.14 nm, for each of which the graphic values of $n_j(\lambda)$ were used at wavelengths $\lambda_1 = 0.4$ μm,

$\lambda_2 = 0.5 \mu\text{m}$, $\lambda_3 = 0.6 \mu\text{m}$, $\lambda_4 = 0.7 \mu\text{m}$, and $\lambda_5 = 0.8 \mu\text{m}$ [48]. As a result, for $h = 168.88$, 260.73 , and 266.14 nm , we obtain the components $L_{\perp}^{(3)} = 0.427$, 0.425 , and 0.438 , respectively. The closeness of these values indicates that the dependence $L_{\perp}(h)$ in the range of variation in the quantity h under consideration is weak.

For the MHPOBC films with thicknesses $h = 168.88$, 260.73 , and 266.14 nm , the above parameters $L_{\perp}^{(3)}$, and the tabulated refractive indices n_j ($\lambda = 0.6326 \mu\text{m}$) [48], the values of σ are 0.687 , 0.551 , and 0.671 , respectively. They are close to the corresponding values for the Cd-A Langmuir films, even though the difference between the components L_{\perp} is significant.

3.1.5. A film of the comblike calamitic liquid-crystal polymer CLLCPz (acrylic copolymer with side mesogenic fragments $-\text{C}(\text{O})\text{O}-(\text{CH}_2)_5-\text{O}-\langle\text{Ph}\rangle-\langle\text{Ph}\rangle-\text{CN}$ and impurities of side fragments $-\text{C}(\text{O})\text{O}-(\text{CH}_2)_5-\text{O}-\langle\text{Ph}\rangle-\text{N}=\text{N}-\langle\text{Ph}\rangle-\text{CN}$ at a concentration of $z\%$) between plane-parallel SnO_2 electrodes [6].

The homeotropic orientation of the director \mathbf{n} was achieved by the orientation of polar side fragments in a low-frequency electric field applied to cell plates. The refractive indices $n_j(\lambda)$ of the CLLCPz films at wavelengths $\lambda_1 = 0.4358 \mu\text{m}$, $\lambda_2 = 0.5461 \mu\text{m}$, and $\lambda_3 = 0.6328 \mu\text{m}$ were measured using a set of optical methods at room temperature for the concentrations $z = 0$ (λ_{1-3}), 10 , and 20% ($\lambda_{2,3}$); these indices were tabulated in [6]. From these data for the sample with $z = 0$, we obtain a value of $L_{\perp}^{(1)} = 0.4058$ and a close value of $\langle L_{\perp}^{(0)} \rangle = 0.4031 \pm 0.0005$, which differs from the component $L_{\perp}^{(1)}$ due to the relatively low accuracy of the refractive indices $n_{\parallel} \pm 0.008$ [6]. For the films with concentrations $z = 0$, 10 , and 20% , the use of the refractive indices $n_j(\lambda_{2,3})$ leads to the components $L_{\perp}^{(0)} = 0.4025$, 0.4039 , and 0.4041 , respectively. The closeness of these values corresponds to the coincidence of the dispersion dependences $n_j(\lambda)$ for the CLLCPz samples with different z [6]. For the CLLCPz films with 4-alkoxy-4'-cyanobiphenyl side fragments, which make the main contribution to the values of Δn and Q , the components L_{\perp} obtained are in good agreement with the experimental values of $L_{\perp} = 0.40-0.41$ for low-molecular nematic liquid crystals 4-alkyl-4'-cyanobiphenyls and 4-alkoxy-4'-cyanobiphenyls [31, 40, 41], which should be expected. At $\lambda = 0.6328 \mu\text{m}$ and $L_{\perp} = L_{\perp}^{(1)}$, the values of $\sigma = 0.333$ and $A = 1.836$ correspond to $\Delta f/\bar{f} = -0.119$ for the CLLCP0 film.

3.1.6. A uniaxial film of the conjugated polymer poly(9,9-dioctylfluorene) (PFO) with $h = 100 \text{ nm}$ and

one free surface on the rubbed orienting polyimide layer deposited on the SiO_2 substrate [11].

For this PFO film, which is in a glassy state at room temperature, the dispersion dependences of the real (n_j) and imaginary (k_j) parts of the complex refractive index were measured by the ellipsometric method in the range $\lambda = 0.25-0.85 \mu\text{m}$ and graphically represented in [11]. The use of the refractive indices $n_j(\lambda)$ in the transparency range of the film at wavelengths $\lambda_1 = 0.466 \mu\text{m}$, $\lambda_2 = 0.50 \mu\text{m}$, $\lambda_3 = 0.60 \mu\text{m}$, $\lambda_4 = 0.70 \mu\text{m}$, and $\lambda_5 = 0.85 \mu\text{m}$ results in the component $L_{\perp}^{(3)} = 0.4527$ and the quantity $\langle L_{\perp}^{(2)} \rangle = 0.4530 \pm 0.0002$ averaged over five values of $L_{\perp}^{(2)}$ for possible combinations of four references λ_i of the set λ_{1-5} .

In the range λ_{1-5} , the PFO film is characterized by a strong dispersion of relatively large values of $\Delta n(\lambda)$, which vary from $\Delta n(\lambda_1) = 0.62$ to $\Delta n(\lambda_5) = 0.217$. Correspondingly, at $L_{\perp} = L_{\perp}^{(3)}$, an increase in the wavelength λ in the range λ_{1-5} is accompanied by a triple increase in the quantity σ from 0.254 to 0.745 with a double increase in the parameter A ($\Delta f/\bar{f}$) from 1.445 (-0.220) to 2.751 (-0.283).

3.1.7. A freely suspended film of the conjugated polymer poly(*p*-phenylene vinylene) (PPV) with $h = 15 \mu\text{m}$ and planar orientation of the director \mathbf{n} (produced by fivefold uniaxial stretching) [12, 13].

For the PPV film, the dependences $n_j(\lambda)$ at room temperature were measured by the interferometric method in the transparency range $\lambda = 0.5556-1.6667 \mu\text{m}$ and graphically represented in [12]. The use of these values of $n_j(\lambda)$ at wavelengths $\lambda_1 = 0.5882 \mu\text{m}$, $\lambda_2 = 0.6250 \mu\text{m}$, $\lambda_3 = 0.7143 \mu\text{m}$, $\lambda_4 = 0.8333 \mu\text{m}$, and $\lambda_5 = 1.0526 \mu\text{m}$ gives the components $L_{\perp}^{(3)} = 0.513$ and $\langle L_{\perp}^{(2)} \rangle = 0.510 \pm 0.002$. The PPV film is characterized by a weak dispersion of very large values of $\Delta n(\lambda)$, which vary from $\Delta n(\lambda_1) = 1.865$ to $\Delta n(\lambda_5) = 1.095$. At $L_{\perp} = 0.510$, an increase in the wavelength λ in the range λ_{1-5} leads to an increase in the quantity σ by a factor of 1.5 from 0.271 to 0.417 with an insignificant increase in the parameter A (decrease in $\Delta f/\bar{f}$) from 1.339 (-0.724) to 1.591 (-0.623); in this case, the value of $\Delta f/\bar{f}$ for the PPV film is two to three times larger than that for the PFO film. Upon changing over from the PFO film to the PPV film, the increase in the component L_{\perp} correlates with the increase in the birefringence Δn .

In [13], the graphic dependences of the components $n_j(\lambda)$ and $k_j(\lambda)$ of the complex refractive index for the PPV film subjected to fivefold stretching ($h = 15 \mu\text{m}$) were obtained from the polarized reflectance and transmittance spectra in the wavelength range $\lambda = 0.2-0.8 \mu\text{m}$ at different temperatures. The use of the

refractive indices $n_j(\lambda)$ at room temperature in the transparency range of PPV at wavelengths $\lambda_1 = 0.54 \mu\text{m}$, $\lambda_2 = 0.58 \mu\text{m}$, $\lambda_3 = 0.62 \mu\text{m}$, $\lambda_4 = 0.70 \mu\text{m}$, and $\lambda_5 = 0.80 \mu\text{m}$ results in the components $L_{\perp}^{(3)} = 0.518$ and $\langle L_{\perp}^{(2)} \rangle = 0.516 \pm 0.001$, which are close to the aforementioned components despite a shorter wavelength range $\lambda_1\text{--}\lambda_5$.

3.2. Optically Negative Media

3.2.1. Planar-oriented films of discotic liquid crystals of pyrene (Py) and benzoperylene (Bp) derivatives [14] in the Col_{hd} phase with $h = 176$ (Py) and 162 (Bp) nm on the poly(tetrafluoroethylene) (PTFE) substrate with one free surface and Col_{hd} –isotropic liquid phase transition temperatures of 92 (Py) and 225°C (Bp).

For the Py and Bp films, the dependences $n_j(\lambda)$ at room temperature in the visible range [14] were obtained from the ellipsometric data and polarized electronic absorption spectra with the use of the Kramers–Kronig relations. For the Py film, the component $L_{\perp}^{(3)} = 0.197$ corresponds to the refractive indices $n_j(\lambda)$ at wavelengths $\lambda_1 = 0.45 \mu\text{m}$, $\lambda_2 = 0.50 \mu\text{m}$, $\lambda_3 = 0.55 \mu\text{m}$, $\lambda_4 = 0.60 \mu\text{m}$, and $\lambda_5 = 0.65 \mu\text{m}$. For the set $n_j(\lambda_{1-4})$, we obtain the component $L_{\perp}^{(2)} = 0.202$. For the Bp film with a narrower transparency range, the refractive indices $n_j(\lambda_{2-5})$ give the component $L_{\perp}^{(2)} = 0.167$. The set $n_j(\lambda_{2-4})$ results in the component $L_{\perp}^{(1)} = 0.176$. The components $L_{\perp}^{(m)}$ for different sets of λ_i agree with each other, even though the accuracy of the refractive indices $n_j(\lambda)$ is low (± 0.03) [14]. For the Bp film with a more perfect planar orientation [14], the values of $L_{\perp}^{(m)}$ coincide with the known component $L_{\perp} = 0.17 \pm 0.01$ obtained using several spectral methods for a more ordered Col_{ho} phase of the liquid-crystal triphenylene derivative [31, 50].

For the Py (Bp) film at the wavelength $\lambda = 0.6 \mu\text{m}$ and $L_{\perp} = L_{\perp}^{(3)}$ ($L_{\perp}^{(2)}$), we obtain large values of $\sigma_d = 0.497$ (0.623) and noticeably different values of $\sigma_{\text{lim}} = 0.619$ (0.810) at $A = 3.031$ (3.353). The ratios $\Delta f_d/\bar{f} = 0.228$ and 0.329 for the Py and Bp films are two to three times larger than those for calamitic liquid crystals with larger values of Δn and L_{\perp} . At the above wavelength λ , an increase in the quantity Δn by a factor of 1.26 upon changing over from the Bp film to the Py film correlates with an increase in the ratio $\Delta f_d/\bar{f}$ by a factor of 1.44.

3.2.2. A uniaxial film of poly(vinyl alcohol) (PVA) with $h = 2.3541 \pm 0.0036 \mu\text{m}$ [8] on the substrate (prepared by the doctor blade technique [9, 49]) with the homeotropic orientation of the director \mathbf{n} . The polymer chains are predominantly oriented in the film

plane, which ensures the relationship $n_{\perp} > n_{\parallel}$ in the visible range.

For the PVA film, the refractive indices $n_j(\lambda)$ at the wavelengths $\lambda_1 = 0.4579 \mu\text{m}$, $\lambda_2 = 0.4880 \mu\text{m}$, $\lambda_3 = 0.5287 \mu\text{m}$, $\lambda_4 = 0.5892 \mu\text{m}$, and $\lambda_5 = 0.6328 \mu\text{m}$ are tabulated with a record accuracy of 10^{-6} [8]. From these data, we obtain the components $L_{\perp}^{(3)} = 0.331907$ and $\langle L_{\perp}^{(2)} \rangle = 0.331905 \pm 0.000019$. This example shows the achievable accuracy in the determination of the component L_{\perp} for a sufficient accuracy of the refractive indices $n_j(\lambda)$. For the PVA film with normal dispersion of the refractive indices $n_j(\lambda)$ in the wavelength range λ_{1-5} , the quantity $|\Delta n| = 0.0023$ is small and does not depend on the wavelength λ [8, 9]. To this correspond a smallness of the ratio $\Delta f_d/\bar{f}$ and its weak change from 0.0022 to 0.0023 with an increase in λ from λ_1 to λ_5 . The quantity σ_d (σ_{lim}) is large and increases from 0.404 (0.405) to 0.460 (0.461); in this case, the values of σ_d and σ_{lim} almost coincide with each other and the value of A changes from 2.324 to 2.532.

A comparison with the corresponding data for the aforementioned discotic liquid crystals demonstrates that, at $\lambda \approx 0.633 \mu\text{m}$, the changeover from the Py film to the PVA film is accompanied by a decrease in the quantity Δn ($\Delta f_d/\bar{f}$) by a factor of 70 (100) and a decrease in the value of σ_d by a factor of only 1.08. Upon changing over from the Bp film to the PVA film at the same wavelength λ , the quantity Δn ($\Delta f_d/\bar{f}$) decreases by a factor of 90 (140) and the value of σ_d increases by a factor of 1.4. Therefore, there is a correlation between the changes in the quantities Δn and $\Delta f_d/\bar{f}$, whereas a direct relation between the quantities Δn ($\Delta f_d/\bar{f}$) and σ_d is absent.

The model with the component $L_j = 1/3$ [32, 36, 37] for the PVA film corresponds to the values of σ_i ($A = 0$), which change from $\sigma_i(\lambda_1) = -0.306$ to $\sigma_i(\lambda_5) = -0.301$, which contradicts the experimental data even in sign. This suggests complete inapplicability of the model under consideration even for anisotropic polymer films with ultimately small values of Δn .

3.2.3. A comblike liquid-crystal polymer K- x [7] (methacrylic copolymer with a fraction x of the side fragments $-\text{C}(\text{O})\text{O}-(\text{CH}_2)_2-\text{N}(\text{CH}_3)-\langle\text{Ph}\rangle-\text{N}=\text{N}-\langle\text{Ph}\rangle^*-\text{CN}$ and a fraction $1-x$ of the side fragments $-\text{C}(\text{O})\text{O}-(\text{CH}_2)_2-\text{O}-\langle\text{Ph}\rangle-\text{C}(\text{O})-\text{N}(\text{H})-\langle\text{Ph}\rangle-\text{N}=\text{N}-\langle\text{Ph}\rangle^*-\text{CN}$, where $\langle\text{Ph}\rangle^*$ is the phenyl ring with the CN substituent in the ortho position with respect to the $\text{N}=\text{N}$ bridge).

K- x films with a submicron thickness and homeotropic orientation of the director \mathbf{n} on glass or fused silica substrates were prepared using the spin-coating technique [7]. The refractive indices of these films were measured at the wavelengths $\lambda_1 = 0.633 \mu\text{m}$ and

$\lambda_2 = 0.780 \mu\text{m}$ with the use of attenuated total reflection spectroscopy, and they were tabulated in [7]. These data make it possible to obtain the component $L_{\perp}^{(0)}$. For the K-0 film with $h = 0.58 \mu\text{m}$, we have the component $L_{\perp}^{(0)} = 0.311$. For the K-0.1 film with $h = 0.780$ and $0.988 \mu\text{m}$, we obtain the components $L_{\perp}^{(0)} = 0.319$ and 0.323 , respectively. The component $L_{\perp}^{(0)} = 0.301$ corresponds to the K-0.3 film with $h = 0.656 \mu\text{m}$. Close values of the component $L_{\perp}^{(0)}$ are characterized by the dependence on the composition and the thickness of the films. However, irrespective of the polymer composition, at a fixed wavelength λ , an increase in the birefringence $|\Delta n|$ in the series K-0.1 ($h = 0.988 \mu\text{m}$) \rightarrow K-0.1 ($h = 0.780 \mu\text{m}$) \rightarrow K-0 \rightarrow K-0.3 is accompanied by a decrease in the component L_{\perp} .

At $\lambda = 0.633 \mu\text{m}$, for the K-0.3 film with $|\Delta n| = 0.110$, the value of $\sigma_d = 0.178$ at $A = 1.474$ corresponds to the ratio $\Delta f_d/\bar{f} = 0.036$. For the K-0.1 film ($h = 0.988 \mu\text{m}$) with a considerably smaller value of $|\Delta n| = 0.034$, we have $\Delta f_d/\bar{f} = 0.012$ and $\sigma_d = 0.190$ at $A = 1.502$. The changeover K-0.3 \rightarrow K-0.1 is accompanied by a threefold decrease in the quantities $|\Delta n|$ and $\Delta f_d/\bar{f}$.

3.2.4. A film of the conjugated polymer PFO with $h = 48 \text{ nm}$ on the SiO_2 substrate with the homeotropic orientation of the director \mathbf{n} (prepared using the spin-coating technique) [11].

For this film, the dependences $n_j(\lambda)$ and $k_j(\lambda)$ were measured by the ellipsometric method in the wavelength range $\lambda = 0.25\text{--}0.85 \mu\text{m}$ [11]. The use of the refractive indices $n_j(\lambda)$ at wavelengths λ_{1-5} presented in Section 3.1.6 results in the components $L_{\perp}^{(3)} = 0.267$ and $\langle L_{\perp}^{(2)} \rangle = 0.274 \pm 0.007$. In the range λ_{1-5} , the PFO film exhibits a strong dispersion of small values of $\Delta n(\lambda)$, which change from $|\Delta n|(\lambda_1) = 0.14$ to $|\Delta n|(\lambda_5) = 0.03$. Correspondingly, at $L_{\perp} = 0.267$, an increase in the wavelength λ in the range λ_{1-5} is accompanied by a sixfold monotonic increase in the quantity σ_d from 0.551 to 3.099 with a fourfold (weak) increase in the value of A ($\Delta f_d/\bar{f}$) from 2.476 (0.142) to 10.221 (0.193).

3.2.5. A film of the conjugated polymer PPV with $h = 160 \text{ nm}$ on the In_2O_3 substrate with the homeotropic orientation of the director \mathbf{n} (prepared using the spin-coating technique) [54].

For this film, the dependences $n_j(\lambda)$ and $k_j(\lambda)$ were measured by the ellipsometric method in the wavelength range $\lambda = 0.30\text{--}0.97 \mu\text{m}$ [54]. In the present work, we used the refractive indices $n_j(\lambda)$ in the transparency range of the film at $\lambda_1 = 0.55 \mu\text{m}$, $\lambda_2 =$

$0.60 \mu\text{m}$, $\lambda_3 = 0.70 \mu\text{m}$, $\lambda_4 = 0.80 \mu\text{m}$, and $\lambda_5 = 0.90 \mu\text{m}$. In view of the anomalous variation in the refractive indices $n_j(\lambda)$ between the wavelengths λ_2 and λ_3 , which is associated with the specific features of the measurements [54] and distorts the true values of $n_j(\lambda_{2,3})$, the system of five equations (10) at $\lambda = \lambda_{1-5}$ for determining the component $L_{\perp}^{(3)}$ has no physical solution. However, the solutions $L_{\perp}^{(2)}$ for all combinations of four wavelengths λ_i of the set λ_{1-5} exist and give an average value of $\langle L_{\perp}^{(2)} \rangle = 0.179 \pm 0.027$, which is considerably smaller than that for the PFO film.

As compared to the PFO film, the PPV film is characterized by a weak dispersion of large values of the birefringence $\Delta n(\lambda)$, which change from $|\Delta n|(\lambda_1) = 0.563$ to $|\Delta n|(\lambda_5) = 0.416$. Correspondingly, for this film at $L_{\perp} = 0.179$, an increase in the wavelength λ in the range λ_{1-5} is accompanied by an irregular weak change in the quantity σ_d from 0.220 to 0.228 with an increase in the value of A (a decrease in the ratio $\Delta f_d/\bar{f}$) from 1.615 (0.242) to 1.753 (0.224); in this case, the ratio $\Delta f_d/\bar{f}$ for the PPV film is larger than that for the PFO film. A decrease in the component L_{\perp} upon changing over from the PFO film to the PPV film correlates with an increase in the quantity $|\Delta n|$.

4. DISCUSSION OF THE RESULTS

As was noted in the Introduction, the general problem in calculating the tensor components L_j in terms of the continuum and lattice models of membranes, Langmuir films, and polymers is the choice of an "adequate" point-polarizable fragment: the entire molecule [1, 2], its subfragments CH_2 [23, 26] or C_2H_4 [22], or other fragments [24, 34]. This approach ignores the anisotropy of bonds forming the molecule, nonlocal character of their polarizability, and imperfection of the orientational order of molecules as a whole and their individual fragments. Therefore, agreement between experimental and calculated refractive indices n_j , which is achieved as a result of the combination of additional approximations (a subjective choice of a subfragment and values of $\bar{\alpha}$ and $\Delta\alpha$ for it among a wide range of the data available in the literature, additive scheme for the calculations of the quantities $\bar{\gamma}$ and $\Delta\gamma$ for the molecule from the data on $\bar{\alpha}$ and $\Delta\alpha$, approximation $S = 1$ for the molecule and its fragments) cannot serve as a criterion of the adequacy of the used components L_j . Moreover, these calculations disregard the dependence of the tensor γ on the phase state of the medium and the limitation from below on the mean molecular polarizability $\bar{\gamma}$ due to the presence of the long-range orientational order of molecules in the media under consideration [30].

Using the proposed method for determining the components L_{\perp} , the polarizability anisotropy $\Delta\gamma$ of the molecule (polymer macromolecule) or its subfragments is not involved in expressions (2)–(4), (9), and (10). The explicit relationship for the polarizability $\bar{\gamma}$ is also not used in formulas (2) for the function b and (9) for the function d , and the limitation of the lowest level on the polarizability $\bar{\gamma}$ [30] is taken into account in formulas (3) and (10) in selecting the physical solutions $L_{\perp}^{(m)}$: the values of L_{\perp} defined by expression (3) are real at $b < b_1$, or in the limitation

$$\bar{\gamma} > \frac{3(\bar{\varepsilon} - 1)}{4\pi r_1 N(\bar{\varepsilon} + 2)}, \quad (16)$$

$$r_1 = 1 + \frac{6Q^2}{(\bar{\varepsilon} + 2)(3 - Q)(3 + 2Q)}.$$

For optically negative media, here, the quantity Q should be replaced by $-Q_d$. Therefore, the obtained values of L_{\perp} are free of prior assumptions associated with the choice of the polarizable fragment, properties of its polarizability, and dependence of the polarizability γ on the phase state of the medium.

For sufficient accuracy of experimental refractive indices $n_j(\lambda)$, the determined components $L_{\perp}^{(m)}$ are in agreement with the averages values of $\langle L_{\perp}^{(m-1)} \rangle$, which indicates the adequacy of approximation (4). In our work, this was demonstrated for different objects with the use of the refractive indices $n_j(\lambda)$ obtained by methods of integrated optics [4, 8], ellipsometry [11], interferometry [12], polarized reflectance and transmittance spectroscopy [13], and refractometry [45]. Owing to the higher accuracy of these methods as compared to polarization spectroscopy, the accuracy of the components $L_{\perp}^{(m)}$ determined from the dependences $n_j(\lambda)$ can be several orders of magnitude higher than that of the components L_{\perp} found from spectral measurements [31, 41, 50]. The high sensitivity of the components $L_{\perp}^{(m)}$ to the dispersion of the quantities $n_j(\lambda)$ and $\Delta n(\lambda)$ can be used for checking the adequacy of the refractive indices $n_j(\lambda)$. For example, for comb-like liquid-crystal polymers K- x ($x = 0.2, 0.4, 1.0$) with the planar orientation (Section 3.2.3), nonphysical anomalous dispersion of experimental values of $|\Delta n|(\lambda)$ in the range $0.633\text{--}0.780\ \mu\text{m}$ [7] corresponds to complex values of $L_{\perp}^{(0)}$ and indicates an insufficient accuracy of the refractive indices $n_j(\lambda)$. The real values of $L_{\perp}^{(0)}$ correspond to the normal dispersion of $|\Delta n|(\lambda)$ in this range for the samples K- x ($x = 0, 0.1, 0.3$).

Let us note the general regularities that are characteristic of changes in the quantities Δn , L_{\perp} , Δf , and σ and are independent of the nature of the objects under investigation. The optically positive media

(Sections 3.1.1–3.1.7) are characterized by the experimental values of L_{\perp} that, in the visible transparency range, correspond to the inequalities $b < 0$, $L_{\perp} > L_{\perp k}$, and $\Delta f < 0$. This agrees with the independent data of spectral methods for calamitic nematics and smectics A [31, 40, 41], as well as with the results of our method used for cholesterics and smectics A [42]. With due regard for expression (2) for the function b and inequalities $r_0 < 1 < r_1$, this leads to the stronger (as compared to relationship (16)) limitations

$$\bar{\gamma} > \frac{3(\bar{\varepsilon} - 1)}{4\pi r_0 N(\bar{\varepsilon} + 2)} > \frac{3(\bar{\varepsilon} - 1)}{4\pi N(\bar{\varepsilon} + 2)}. \quad (17)$$

The experimental values of L_{\perp} for optically negative media (Sections 3.2.1–3.2.5) correspond to the inequalities $d < 0$, $L_{\perp} < L_{\perp k}$, and $\Delta f_d > 0$. They agree with the data of independent spectral methods for discotics Col_{ho} [50]. With allowance for expression (9), this results in limitations similar to limitations (17) in which r_0 is replaced by r_{0d} . Inequalities (17) suggest that formula (15) is incorrect for the objects under consideration. In the isotropic approximation $\Delta f = b = 0$, the left-hand inequality in (17) transforms into an equality, whereas the right-hand inequality is retained. This implies that the isotropic tensor $f_j = (\bar{\varepsilon} + 2)/3$ [29, 55] widely used in optics of liquid crystals is incorrect.

Over the entire transparency range of the media under investigation, irrespective of their optical sign, the relationships σ and $\sigma_d > 0$ and $A > 1$ hold true. In this case, a change in the quantity Δn by several orders of magnitude leads to an insignificant change in the value of A . As a consequence, there is a correlation between changes in the quantities Δf and $\Delta n \propto Q$ in formulas (7) and (13). However, there is no correlation between the changes in the quantities Δf and σ ; in this case, objects with small values of Δn (biomembranes, Langmuir films, anisotropic films of conventional and conjugated polymers) are characterized by large values of σ (Sections 3.1.1, 3.1.2, 3.2.2, 3.2.4). This indicates that the widespread opinion regarding the correctness of the approximation $\sigma = 0$ for media with small values of Δn is wrong. For a particular object, a strong decrease in the quantity $\Delta n(\lambda)$ with an increase in the wavelength λ can be accompanied by a strong increase in the quantity σ (Sections 3.1.2, 3.1.6, 3.2.4).

A correlation between the changes in the quantities L_{\perp} and Δn for different media due to the difference in the chemical and electronic structures of molecules forming these media is of the most interest. For optically positive (negative) media, a decrease in the birefringence Δn is accompanied by a decrease in the component $L_{\perp} > L_{\perp k} > 1/3$ (an increase in the component $L_{\perp} < L_{\perp k} < 1/3$), which corresponds to the isotropization of the tensor L . Ultimately high values of $L_{\perp} \leq 0.5$ ($L_{\perp} \geq 0.5$) were obtained for planar-oriented (uniaxially stretched) films of PFO (PPV) conjugated polymers. A small (but beyond the limits of the error of the

method used) difference of the components $L_{\perp} = 0.510\text{--}0.516$ from 0.5 for the stretched PPV films [12, 13] can be associated with the small biaxiality of the films in the XY plane normal to the stretching direction $Z \parallel \mathbf{n}$ [56] due to the nonequivalence of the XZ plane of the film and the perpendicular YZ plane. On the one hand, the components L_{\perp} for conjugated polymers are consistent with model (1) with $L_{\perp} \approx 0.5$ at $l \gg D$ and justify its use in the theory of electronic and optical properties of these objects [13, 38, 39]. On the other hand, since the conjugated polymer molecules are conductive in character at an infinite length of the conjugated chain and the orientation is such that $\mathbf{l} \parallel \mathbf{n}$, the equality $E_{\parallel}^{(\text{loc})} = E_{\parallel}$ (corresponding to the value of $L_{\parallel} = 0$) should hold true. The values of $L_{\parallel} > 0$ ($L_{\perp} < 0.5$) for real conjugated polymers can be explained by the finite length of "conformational subunits" [52] forming the polymer molecule and the finite chain of conjugation for monomer units involved in these subunits. Therefore, the closeness of the components L_{\perp} for the PFO and PPV conjugated polymers to the limiting value calculated from formula (1) may be accidental.

A gradual decrease in the birefringence Δn upon changing over from the smectics $Bm.n$ and BPh.4 (Section 3.1.3) with a chain of strong π -electron conjugation of molecular fragments to the smectic MHPOBC (Section 3.1.4) and the liquid-crystal polymer CLLCPz (Section 3.1.5) with a weaker conjugation of fragments and then to the lipid membrane and Langmuir films (Sections 3.1.1, 3.1.2) without conjugation of molecular fragments is accompanied by a monotonic decrease in the component L_{\perp} , which approaches 1/3. This agrees with the data of independent spectral methods on the isotropization of the tensor L for nematics [57] and anisotropic polymer films [58] with a decrease in the quantities Δn and $\Delta\gamma$. In our work, this effect was also established for optically negative media. For the PVA film (Section 3.2.2) with the record small value of Δn , the high accuracy of the refractive indices $n_j(\lambda)$ made it possible to reveal the minimum difference between $L_{\perp} = 0.3319$ and 1/3 and the limiting value of $A_{\text{lim}} > 2$ in expression (7).

Therefore, the above analysis clearly demonstrates that the use of modern models for the calculations of the tensor components L_j that ignore the specific features of the electronic structure of molecules (nonlocality of the molecular polarizability, polarizability distribution over the molecular volume, π -electron conjugation of fragments) cannot ensure agreement between the calculated and experimental components L_{\perp} . For example, the component $L_{\perp} = 0.363$ for the lipid membrane POPC10 with $h = 5.2$ nm (Section 3.1.1) differs substantially from the component $L_{\perp} = 0.443$ calculated from formula (1) in [2]. The microscopic calculations [23] of the components L_j for the membrane (with $h = 5.15$ nm) consisting of hydrocarbon molecules result in the component $L_{\perp} = 0.498$ ([23, Table 2]) close to the component $L_{\perp} =$

0.491 calculated from formula (1) with $D = 1$ nm [23] and lead to the inequality $\Delta n < 0$ instead of the experimentally observed inequality $\Delta n > 0$ [1].

5. CONCLUSIONS

In conclusion, we note a number of important points. The proposed optical method can be used to determine the tensor components L_j for uniaxial molecular films of different nature with a planar or homeotropic orientation of the optical axis. The film thickness can vary from several nanometers to several tens of microns. The accuracy in determining the components L_{\perp} is governed by the accuracy in measuring the refractive indices $n_j(\lambda_i)$ at several wavelengths λ_j in the visible transparency range and can be as high as 10^{-5} . In the present work, this made it possible for the first time to reveal subtle features of the change in the components L_{\perp} with a small change in the concentration of impurity molecules in the lipid membrane, replacement of the substrate for the multilayer Langmuir films, two-dimensional crystallization of smectic layers upon the SmA–SmB transition, and change in the thickness of freely suspended smectic A films. Moreover, we established that relation (14) has a universal character for uniaxial orientationally ordered molecular media of all types irrespective of the presence, symmetry, scale (short-range or quasi-long-range), and dimension (one-dimensional smectic, two-dimensional discotic) of the positional ordering of molecules.

Relation (14), which is invariant with respect to the nematic (cholesteric)–SmA and SmA–SmB phase transitions, means that the positional ordering of molecules manifests itself in the components L_j as a result of the change in the orientational ordering of molecules due to the relation of the smectic and hexatic order parameters to the orientational (nematic) order parameter of molecules. The experimental values of L_{\perp} indicate that the continuum [1, 2, 32–34] and microscopic [22–24, 26, 35] model approaches are inapplicable to calculating the components L_j . These models account for the anisotropy of the translational distribution of the molecules and their fragments but leave the choice of point-polarizable subfragments arbitrary and disregard the following factors: the nonlocality of the molecular polarizability, specific features of its distribution over the molecular volume, the presence or absence of π conjugation of molecular fragments, the dependence of the molecular polarizability tensor γ on the phase state of the medium, and the limitation from below on the mean polarizability $\bar{\gamma}$ due to the presence of orientational ordering (optical anisotropy) of the medium. The importance of these factors is indicated by the revealed dependence $L_j(\Delta\gamma)$ (characteristic of all the objects under investigation) on the molecular polarizability anisotropy $\Delta\gamma$

(birefringence Δn) for a fixed temperature and orientational ordering of molecules.

The proposed method is free of prior assumptions regarding the unobservable molecular properties (the mean polarizability $\bar{\gamma}$ [27–29] and oscillator strengths of molecular transitions [31, 41, 57]), which underlie the theoretical [27] and experimental (spectral [31, 41, 57]) methods for determining the components L_j in liquid crystals. This is important for obtaining objective information on the properties of molecules and their changes in the anisotropic medium during molecular self-organization. In particular, the established anisotropy $\Delta f < 0$ ($\Delta f > 0$) for optically positive (negative) films results in limitation (17) on the mean polarizability $\bar{\gamma}$. However, the model theories based on the prior assumptions regarding the mean polarizability $\bar{\gamma}$, which is independent of the phase state of liquid crystals or defined by expression (15), lead to the inequality $\Delta f > 0$ ($\Delta f < 0$). In terms of the method under consideration, the coefficients a_0 – a_m of polynomial (4) and the functions $b(\lambda, T)$, $d(\lambda, T)$, and $\bar{\gamma}(\lambda, T)$ are also determined in addition to the components $L_{\perp}^{(m)}(T)$. This allows one to control the subtle features of the change in the function $\bar{\gamma}(\lambda, T)$ with changes in the short-range and long-range orders of molecules [30], film composition, and properties of the medium bordering the film.

Data on the dispersion of the refractive indices $n_j(\lambda)$ for molecular films are very scarce in the literature. Therefore, in our work, we did not analyze objects with unknown dependences $n_j(\lambda)$. These are homeotropically oriented uniaxial surface layers of liquids at the boundary with vacuum [59] or the substrate [60], as well as the anisotropic monomolecular layers adsorbed on substrates. The local-field effects in adsorbed layers have been considered in a large number of theoretical works (see, for example, [61–63] and references therein). For freely suspended films of smectics A and B, only the dependences $n_{\perp}(\lambda, T)$ have been investigated in sufficient detail [64, 65]. The new capabilities of refractometry revealed in this study can stimulate the development of this method with the aim of increasing the accuracy, extending the spectral range, and applying it to study the structure and properties of natural self-assembled and artificial molecular ensembles over a wide range of scales.

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