Effects of the local field of a light wave in the molecular optics of liquid crystals

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The current state of the problem of the local field of a light wave in liquid crystals is analyzed in the theoretical and experimental aspects. The fundamental properties of the local-field tensor are studied within the framework of various theoretical approaches. A connection is established between the anisotropy of the local field and the molecular and macroscopic parameters of liquid crystals, their orientational and translational order, and the character of the intermolecular correlations. The effects of the local field in refractometry, absorption spectroscopy, and Raman scattering in liquid crystals are discussed. The strong influence of the anisotropy of the local field on the moments of the orientational distribution function (the order parameter), as determined from molecular-optics experiments, the molecular susceptibility tensors, and the spectrum of intrinsic and impurity absorption and other characteristics of liquid crystals are studied. Experimental methods of determining the parameters of the local field in liquid crystals are examined.

INTRODUCTION

The intensive development of the phenomenological theory of liquid crystals (LCs) in recent years has led to a successful description of the fundamental types of response of LCs to external agents that are used in practice.[1–4] The expansion of the field of application of LCs has required the elucidation of the molecular foundations of the physical characteristics of these materials and the development of a molecular-statistical theory of mesophases.[5–6] It has also become clear that the nature of the phase transitions in LCs involves the subtle balance of the intermolecular forces, which depend on the structural features and the physicochemical properties of the molecules,[7–9] while the change in the molecular parameters (conformation, electronic structure, polarizability, etc.) in phase transitions occurs in mutual correlation with the change in the parameters of long-range orientational and translational order of the molecules in mesophases of different types.[9–12,102] The molecular-optics and spectral methods of study, which yield information both on the molecular parameters that directly determine the physical properties of the LCs (linear and nonlinear susceptibilities, energy spectrum, electronic structure, and characteristics of the anisotropic intermolecular interaction), and on the structure and dynamics of LCs (order parameters, their dispersion, orientational distribution functions, molecular diffusion coefficients, relaxation parameters, etc.), have developed rapidly.

However, the relative simplicity and high accuracy of the methods of molecular optics are compensated by the difficulty of obtaining quantitative information on the structure and the molecular parameters of LCs, owing to the need to take account of the effects of the local field (LF) of the light wave in interpreting the experimental data. We must note that in the case of LCs one cannot directly use the rich experience amassed in the microscopical theory of the optical properties of crystals,[13–15] since LCs lack a space lattice, while strong fluctuations exist in the position and orientation of molecules. On the other hand, the anisotropy of the medium and the concomitant strong orientational correlations of the molecules lead to substantial differences between LCs and isotropic liquids, for which also a rather well developed theory exists.[16,17] Owing to the complexity of LCs as objects of theoretical and experimental study, there has been a lack until recently of molecular-statistical methods of describing their optical properties while taking account of the anisotropy of the LF, as well as of methods of determining the parameters of the LF from the experimental data. This has led to the propagation in the physics literature on LCs of a large number of model and semiempirical approaches to the problem of the LF that often contradict one another and lead to nonphysical conclusions from the experimental data. All of this has hindered the development of molecular-optics methods of studying LCs and of the theory of these objects.

However, in the past several years rather consistent methods have been developed for theoretical description and taking account of the effects of the local field in LCs, as well as methods of determining the parameters of the LF in these objects from experimental data. The known effects have been explained, and new ones have been predicted and found involving the features of the local field in LCs. Their properties have been elucidated with a large number of objects. The proposed theoretical and experimental methods can be used to study also other partially ordered molecular media, including polymers, ensembles of amphiphilic molecules, and Langmuir-Blodgett films, ordered biological structures, etc.

The aim of this review is to analyze the current state of the problem of the LF and the concomitant problems of the molecular optics of LCs on the theoretical and the experimental levels. The first part discusses the fundamental properties of the LF tensor in LCs within the framework of different theoretical approaches, the connection is established between the anisotropy of the LF and the molecular and macroscopic parameters of LCs, their orientational and translational order, and the character of the intermolecular correlations. The physical meaning of the approximations on which the different semiphenomenological models are based is elucidated, and the limits of applicability of the latter are indicated. The second part is devoted to analyzing the effects of the LF in refractometry, absorption spectroscopy, and Raman scattering in LCs. The influence of the anisotropy of the LF on the molecular and structural parameters of

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the LF in LCs determinable experimentally is discussed. The third part examines the experimental methods of determining the parameters of the LF in LCs.

1. THE LOCAL FIELD OF A LIGHT WAVE IN A LIQUID CRYSTAL

In an optically continuous condensed medium in which the distances between the molecules are comparable with the dimensions of the molecules themselves, the amplitude E_l of the local field of the light wave acting on them differs from the amplitude E of the macroscopic field in the medium. Owing to the finite dimensions of the molecules, the field E_l is obtained by averaging the microfield over the volume occupied by the given molecule under the condition that one excludes from this microfield the field created by the molecule itself.[18] The mean macroscopic field $\mathbf{E}$ is obtained from the total microscopic field by averaging over the ensemble. The difference between the fields $\mathbf{E}_l$ and $\mathbf{E}$ leads to the so-called local-field effects, many of which are known and have been studied in crystals[13-15] and liquids.[16,17,19]

In the liquid-crystal case the most significant corrections to the local field of the light wave are those that must be taken into account for quantitative, and in a number of cases, even qualitative interpretation of the experimental data obtained by the various optical methods. The magnitude and form of these corrections depend on the concrete model of the local-field tensor $\hat{f}$. Here the use of the different models proposed in the literature for calculating, e.g., the anisotropy of the polarizability of the molecule $\Delta\gamma$, from refractometric data lead to values of $\Delta\gamma$ differing severalfold,[71,87] while the discrepancy in the values of the order parameter S can reach several tens of percent.[2,27,89]

The existence of long-range orientational order in a LC leads to a macroscopic anisotropy of the medium. Therefore the local field in a LC generally also must be anisotropic. Neglect of this anisotropy leads to the appearance of nonphysical regions of the anomalous dispersion of the component γ_i in the region of transparency of the LC.[6] When one uses the methods of Raman light scattering[47] and two-photon absorption,[51] it can also lead to a sign change in the moment $\langle P_4\rangle$ of the orientational distribution function[47] or to a nonphysical temperature dependence of this parameter.[51] We see even with these examples that inadequate models of the local field often do not allow even a qualitative joint interpretation of the results of the different optical methods and the obtaining of reliable quantitative information within the framework of a single method. Thus, to describe the LF in a liquid crystal, it does not suffice to use some particular semiphenomenological models. One must conduct a microscopical treatment in as great detail as possible, despite the evident complexity of the problem. Part of the questions that arise in such a treatment can be posed by analogy with the simpler case of molecular crystals. For example, an exact microscopical calculation of E_l in molecular crystals requires one to take simultaneous account of such factors as the contribution of the higher multipoles to the molecular polarization,[13] the nonlocality of the molecular polarizability,[15] and the renormalization of the effective polarizability of the molecules owing to interaction with the nearest coordination shell.[20] At the same time, many features of the LF in LCs have no analogy in either the theory of liquids or in the theory of crystals.

1.1. The effective local field and the lorentz tensor in a liquid crystal

A very simple description of the properties of the local field can be obtained in the case of an ideal molecular crystal with one molecule in the unit cell. The polarization $\mathbf{P}$ of such a crystal in the molecular point-polarizability approximation has the form

$$\mathbf{P} = N\hat{\gamma}E_L = N\hat{\gamma}(\mathbf{E} + 4\pi\hat{L}\mathbf{P}), \tag{1.1}$$

Here the local field $\mathbf{E}_l$ is related to the polarization by means of the Lorentz tensor $\hat{L}$, which depends on the crystal lattice structure; $\hat{\gamma}$ is the tensor of the effective polarizability of the molecule in the medium, and N is the number of molecules per unit volume.

The properties of $\mathbf{E}_l$ vary substantially upon going from molecular to liquid crystals, in which the field $\mathbf{E}_l(\mathbf{r}_i)$ acting on the molecule is a fluctuating quantity that depends on the random positions and orientations of the surrounding molecules. This field induces in the molecule the random dipole moment

$$\mathbf{p}_i = \hat{\gamma}(\theta_i)\,\mathbf{E}_L(\mathbf{r}_i), \tag{1.2}$$

Here $\hat{\gamma}(\theta_i)$ is the polarizability tensor of the molecule i, which depends on its orientation θ_i. Moreover, the experimentally measurable polarizability of the liquid crystal

$$\mathbf{P} = N\langle\mathbf{p}_i\rangle = N\langle\hat{\gamma}(\theta_i)\,\mathbf{E}_L(r_i)\rangle \neq N\langle\hat{\gamma}(\theta_i)\rangle\langle\mathbf{E}_L(\mathbf{r}_i)\rangle \tag{1.3}$$

depends on the correction between the local field and the polarizability tensor of the molecule, and is not expressed in terms of the mean local field $\langle\mathbf{E}_L(\mathbf{r}_i)\rangle$. Comparison of Eqs. (1.1) and (1.3) shows that one cannot draw an analogy between the local field in crystals and the mean local field in LCs, since the latter does not enter into the expressions for the mean microscopical polarization, the permittivity, and other parameters. On the other hand, taking a microscopical account for each molecule of the LC of the fluctuating tensor $\hat{\Phi}(E_i = \hat{\Phi}E)$ corresponding to it considerably complicates the difficulties noted above in taking consistent account of an entire set of factors. Further, one must take account of the correlations of the molecules caused by steric and dispersion intermolecular interactions.[22,23]

At the same time, one can introduce in a liquid crystal an effective nonfluctuating local field $\mathbf{E}_{\rm eff}$ and an effective Lorentz tensor $\hat{L}_{\rm eff}$ such as to allow keeping and using expressions of the type of (1.1) and thus describing the optical properties of liquid and solid crystals in one common language. Let us define the field $\mathbf{E}_{\rm eff}$ as the nonfluctuating electric field that induces in the individual molecule i the dipole $\mathbf{p}_i$ such that its mean value equals the true mean dipole $\langle\mathbf{p}_i\rangle$ induced by the fluctuating local field $\mathbf{E}_l(\mathbf{r}_i)$:

$$\mathbf{p}_i^* = \langle\hat{\gamma}(\theta_i)\rangle\,\mathbf{E}_{\rm eff} = \langle\mathbf{p}_i\rangle = \langle\hat{\gamma}(\theta_i)E_L(\mathbf{r}_i)\rangle. \tag{1.4}$$

Now we can introduce also the effective Lorentz tensor by analogy to (1.1):

$$\mathbf{E}_{\rm eff} = \mathbf{E} + 4\pi\hat{L}_{\rm eff}\mathbf{P} \tag{1.5}$$

and the effective local-field tensor $\hat{f}$, which is defined by the relationship $\mathbf{E}_{\rm eff} = \hat{f}\mathbf{E}$. This definition of the effective quantities $\mathbf{E}_{\rm eff}$, $\hat{L}_{\rm eff}$, and $\hat{f}$[23-25] corresponds to the phenomenological approach[21,26,27] to determining the form of the tensor $\hat{f}$, in

which the difference between the local fluctuating fields acting on different molecules is neglected.

In line with the definitions (1.4) and (1.5), the effective tensors $\hat{f}$ and $\hat{L}_{\text{eff}}$ are macroscopic quantities. That is, they can be represented in the form of an average over the ensemble of certain functions of the microscopical variables. As is well known, the symmetry of such averaged quantities is determined only by the macroscopic symmetry of the medium (although the short-range order in the orientation of the molecules can have a lower symmetry). Thus, in a uniaxial LC the tensor $\hat{f}$ is uniaxial and has the components

$$f_j = 1 + L_j(\varepsilon_j - 1) \quad (j = \parallel, \perp) \tag{1.6}$$

for a polarization of the light wave parallel and perpendicular to the optic axis; here the ε_j are the components of the permittivity tensor of the LC in the optical frequency range.

The introduction of the effective local field enables one to treat a liquid crystal as an ensemble of identical molecules averaged over the possible set of orientations. The analysis of the optical properties of LCs based on the formulas taken from the well developed theory of crystals proves valid if we take $E1$ and $\hat{L}$ to be the corresponding effective quantities. At the same time, one must always take account of the difference between the effective and microscopical local fields in a liquid crystal.

For nematic and uniaxial smectic LCs, the relation of the components ε_j to the components γ_j and f_j has the form

$$\varepsilon_j - 1 = 4\pi N f_j \gamma_j, \tag{1.7}$$

$$\gamma_\parallel = \bar{\gamma} + \frac{2}{3} S\Delta\gamma + \frac{1}{3} G\Delta\gamma', \quad \gamma_\perp = \bar{\gamma} - \frac{1}{3} S\Delta\gamma - \frac{1}{6} G\Delta\gamma', \tag{1.8}$$

Here we have used the notation

$$\bar{\gamma} = \frac{1}{3}(\gamma_{xx} + \gamma_{yy} + \gamma_{zz}),$$
$$\Delta\gamma = \gamma_{zz} - \frac{1}{2}(\gamma_{xx} + \gamma_{yy}), \tag{1.9}$$
$$\Delta\gamma' = \gamma_{yy} - \gamma_{xx}.$$

The orientational order parameters

$$S = S_{zz}, \quad G = S_{yy} - S_{xx} \tag{1.10}$$

of biaxial molecules in a uniaxial liquid crystal are expressed in terms of the components of the matrix:[1]

$$S_{ii} = \frac{1}{2}\langle 3\cos^2\theta_{in} - 1\rangle \quad (i = x, y, z), \tag{1.11}$$

Here θ_{in} is the angle between the ith axis of the intrinsic coordinate system of the tensor γ and the director **n** of the liquid crystal.

We note that the parameter G, which differs from zero only for biaxial molecules, has no relation to macroscopic biaxiality of the liquid crystal. Actually the parameter G characterizes the preferential orientation of one of the short axes of the biaxial molecule with respect to the plane formed by the director **n** and the long axis **a** of the molecule. With respect to this plane the orientational ordering of the molecules is actually biaxial. However, the system lacks long-range order in the orientation of such planes (in the laboratory system of coordinates) for different molecules, so that only the uniaxial symmetry of a nematic LC is conserved after averaging over the ensemble.

In a cholesteric LC one can introduce[28] the effective uniaxial tensor $\hat{f}_x$ in the coordinate system of the optic axis normal to the quasinematic planes within whose limits the uniaxial tensor $\hat{f}_i$ is defined. The relationship between the anisotropy $\Delta f = f_\parallel - f_\perp$ of these tensors has the form[29]

$$\Delta f_x = -\frac{1}{2}\Delta f_{\text{H}}. \tag{1.12}$$

and it does not depend on the concrete form of the tensors f_x and $\hat{f}_i$.

1.2. General properties of the effective Lorentz and local-field tensors

In line with (1.4)–(1.7), the influence exerted on an individual molecule by its close neighbors, which depends on the intermolecular correlation,[20] formally takes account of the difference between the effective polarizability γ and the polarizability α of the molecules in the gas. For the isotropic phase of a liquid crystal as a homogeneous liquid dielectric, in the dipole approximation the macroscopic expression for f has the form:[30]

$$f = \frac{\rho}{\varepsilon - 1}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T, \tag{1.13}$$

Here ρ is the density. If we take into account the high accuracy of fulfillment of the following relationships[31] for LCs and isotropic phases of mesogens:

$$\left(\frac{1}{\rho}\frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2}\right)_{\text{LCs}} = \left(\frac{1}{\rho}\frac{\varepsilon - 1}{\varepsilon + 2}\right)_i = \text{const}, \tag{1.14}$$

where $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$, then we obtain from (1.13) the well known Lorentz formula

$$f = \frac{1}{3}(\varepsilon + 2). \tag{1.15}$$

The condition (1.14) for applicability of Eq. (1.15) to liquids is equivalent to the assumption of independence of the mean value $\bar{\gamma}$ in (1.9) of the density, since when $S = 0$, Eqs. (1.7) and (1.15) imply the Lorentz-Lorentz (L-L) formula[18]

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)_i = \frac{4\pi}{3} N\bar{\gamma}. \tag{1.16}$$

Equations (1.5)–(1.7) are formally analogous to the corresponding expressions in the theory of the optical properties of crystals. Therefore we can say by analogy with crystals that the anisotropy of the tensor $\hat{L}$, $\tau = (L_\parallel - L_\perp)/3$ characterizes the structural anisotropy of the medium. In the case of liquid crystals the structural anisotropy is determined mainly by the anisotropy of the intermolecular correlations. However, we shall see below that the relation between the orientational and translational degrees of freedom has the result that the anisotropy of the Lorentz tensor depends also on the optical anisotropy of the liquid crystal $\Delta\varepsilon$. By using the parameters τ and $\Delta\varepsilon$, we can write Eq. (1.6) in the form[27]

$$\bar{f} = 1 + L(\varepsilon - 1) + \frac{2}{3}\tau\Delta\varepsilon, \tag{1.17}$$

$$\Delta f = \bar{L}\Delta\varepsilon + 3\tau(\bar{\varepsilon} - 1) + \frac{1}{3}\Delta\varepsilon, \tag{1.18}$$

Hence we see that the structural and the optical anisotropy

of the LC contribute to the mean value $\bar{f}$, with this contribution always being negative ($\tau < 0$) and small in comparison with the isotropic component. The magnitude and sign of the anisotropy Δf are determined by the balance of the contributions of the optical and the structural anisotropy of the medium. In the first approximation in $\Delta\varepsilon$ these contributions enter into (1.18) additively, which is a consequence of the overall expression (1.6), according to which the anisotropy of the tensor of the effective local field in a LC can arise both from the anisotropy of the Lorentz tensor $\hat{L}$ and directly from the optical anisotropy $\Delta\varepsilon$. The mutual compensation of these contributions under the condition

$$\tau = \tau_k = -\frac{\bar{L}\Delta\varepsilon}{3\,[\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)]} \tag{1.19}$$

leads to isotropization of the tensor $\hat{f}$:

$$f_{\parallel,\perp} = \bar{f} = 1 + \bar{L}\,(\bar{\varepsilon} - 1) - \frac{2\bar{L}\,(\Delta\varepsilon)^2}{9\,[\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)]}. \tag{1.20}$$

In order to take the limit (1.17) in (1.15), we must set $\bar{L} = 1/3$, which is fulfilled also within the framework of the continuum,[27,32,33] the lattice,[21,33–35] and the semimicroscopical[36–38] approaches to calculating the effective tensor $\hat{L}$ in a liquid crystal. In this case, instead of (1.20), we obtain[27]

$$f_{\parallel,\perp} = \frac{\bar{\varepsilon} + 2}{3} - \frac{2\,(\Delta\varepsilon)^2}{27\,[\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)]}. \tag{1.21}$$

The expression (1.24) coincides with the empirical formula of Vuks[31,39]

$$f = \frac{1}{3}\,(\bar{\varepsilon} + 2), \tag{1.22}$$

which is widely used in optical and spectral studies of LCs upon neglecting the second term in (1.21), which is small in comparison with the parameter $(\Delta\varepsilon/\bar{\varepsilon})^2$.

The general properties of the tensors $\hat{L}$ and $\hat{f}$ can be elucidated[40] on the basis of empirical facts that have been confirmed for a large number of objects. For example, for uniaxial LCs the proportionality $\Delta\varepsilon \sim \rho S$ (Refs. 6, 41) is well known in the optical region. Upon using the relationship[27]

$$\Delta\varepsilon = 4\pi N\left[\bar{\gamma}\Delta f + S\Delta\gamma\left(\bar{f} + \frac{1}{3}\Delta f\right)\right], \tag{1.23}$$

and taking account of the fact that $\Delta f \ll 3\bar{f}$, we have

$$\Delta f \sim \Delta\varepsilon \sim S. \tag{1.24}$$

Upon writing (1.18) in the form

$$\Delta f = \bar{L}\Delta\varepsilon\left(1 - \frac{\tau}{\tau_k}\right), \tag{1.25}$$

we obtain from (1.24)

$$\bar{L}\left(1 - \frac{\tau}{\tau_k}\right) = \text{const}, \tag{1.26}$$

or, upon neglecting a possible weak dependence $\bar{L}(T)$, we have

$$\tau(S) = \text{const}\cdot\tau_k(S). \tag{1.27}$$

Since in the optical region we usually have $\Delta\varepsilon \ll 3(\bar{\varepsilon} - 1)$, then to good accuracy Eqs. (1.19) and (1.27) imply that

$$\tau \sim \Delta\varepsilon \sim S. \tag{1.28}$$

For a fixed liquid crystal the parameter τ is only a function of the temperature, while τ_k depends also on the wavelength λ owing to the dispersion of the components $\varepsilon_{\parallel,\perp}(\lambda)$. Hence, at a certain value $\lambda = \lambda_0$ the equation $(\tau_k(\lambda_0) = \tau$ can hold, together with the spectral isotropization $\Delta f/(\lambda_0) = 0$ of the effective tensor f.[40,42,43] Comparison of (1.25) with (1.27) shows that the value of λ_0 that corresponds to const = 1 is the same for the entire temperature interval of the mesophase. Owing to the normal dispersion of the parameters $\Delta\varepsilon$ and $|\tau_k|$ when $\lambda \gtrless 0$, we have const $\gtrless 1$ and $\Delta f \lessgtr 0$ in (1.27). The isotropic approximation (1.21), (1.22) holds in the vicinity of λ_0. With strong dispersion of $\tau_k(\lambda)$, this region is narrow,[40,43] while for a LC with weakly polarizable molecules and a small birefringence, the approximation $\Delta f = 0$ can be justified over the broad region $\lambda \gtrless 0$.[29]

The mean value of $\bar{f}$ is mainly determined by close-range order effects, and it weakly depends on S and on the phase state of the liquid crystal. According to (1.24) and (1.27), the anisotropy Δf depends on the long-range order of the LC, just like the difference of the ratio $f_\perp/f_\parallel$ from unity. This is important to note, since in studying the orientational order of a liquid crystal by the methods of infrared[29,35,44,45] and ultraviolet spectroscopy,[2,11,26,35] and by Raman scattering,[46–49] luminescence,[50] two-photon absorption,[51] and optical harmonic generation,[52,53] taking account of the anisotropy of the local field is reduced to taking account of the difference of $f_\perp/f_\parallel$ from unity, which actually corresponds to taking account of long-range order effects. We obtain from (1.4), (1.7), and (1.8) the relationship[29]

$$\frac{f_\perp}{f_\parallel} = \frac{\varepsilon_\perp - 1}{\varepsilon_\parallel - 1}\,\frac{1 + (2S\Delta\gamma/3\bar{\gamma}) + (G\Delta\gamma'/3\bar{\gamma})}{1 - (S\Delta\gamma/3\bar{\gamma}) - (G\Delta\gamma'/6\bar{\gamma})}, \tag{1.29}$$

This does not depend on the concrete form of $\hat{f}$ and establishes the connection between the anisotropy of the local field and the optical anisotropy of the liquid crystal, the anisotropy of the polarizability of the molecules, and their orientational order. This implies that the tensor $\hat{f}$ becomes isotropic as the birefringence of the LC and the anisotropy of polarizability are decreased owing to a change in the electronic structure of the molecules while their geometric anisotropy and orientational order are maintained. This effect, which is new in the optics of anisotropic molecular media, and was first observed experimentally in Ref. 29, substantiates the earlier assumptions of a small anisotropy of the local field in nematic[54,55] and cholesteric liquid crystals[28,56,57] having a small optical anisotropy. In the region $f_\perp/f_\parallel \sim 1$ the sign of Δf can change upon a change in the chemical structure of the mesogenic molecules, as was observed[11] for a liquid crystal with extremely small values of the birefringence Δn. These consequences of (1.29) are valid also for other uniaxial orientationally ordered molecular media such as stretched polymer films, liquid-crystalline polymers, layers of surface-active substances, cell membranes, etc.

For the form (1.6) of the tensor $\hat{f}$, Eq. (1.29) implies that, for a fixed anisotropy of form and orientational order of the molecules, and change in the parameters $\Delta\varepsilon$ and $\Delta\gamma$ owing to a change in the electronic structure of the mole-

cules, the anisotropy of the tensor $\hat{L}$ must vary according to:[58]

$$\tau = \tau_k \left[1 + \frac{\bar{f}\,[(\varkappa_2/\varkappa_1) - 1]}{\bar{L}\,(\bar{\varepsilon} - 1)\,(1 + \varkappa_2 - 2\varkappa_1\varkappa_2)} \right], \tag{1.30}$$

Here we have used the notation

$$\varkappa_1 = \frac{\Delta\varepsilon}{3\,(\bar{\varepsilon} - 1)}, \quad \varkappa_2 = \frac{\Delta\gamma S}{3\bar{\gamma}}. \tag{1.31}$$

The isotropization of the tensor $\hat{L}$ found in Refs. 11, 29, and 43 by different methods shows that the tensor $\hat{L}$ is not only determined by the shape of the molecule and other structural characteristics of the LC, but it depends on the anisotropy of the polarizability $\Delta\gamma$ and the features of the electronic structure of the molecules.

We note that all the approaches existing in the literature lead to expressions for the effective local field, which naturally reduce to the common form (1.6), so that these approaches differ only in the methods of calculating $\bar{L}$.

1.3. Continuum and lattice models

The natural way to construct a simple model theory of the refractive indices of a liquid crystal consists in generalizing the continuum model of the spherical cavity of Lorentz to the case of an anisotropic liquid. Here, in the simplest case, one maintains a spherical cavity of spherical form and takes account only of the optical anisotropy of the medium. One can formally generalize the Lorenz-Lorentz relationship for an isotropic medium to the case of an LC by replacing the isotropic qualities ε and γ with the corresponding components. As a result one obtains the anisotropic local-field tensor:[74,75]

$$f_\alpha = \frac{1}{3}(\varepsilon_\alpha + 2). \tag{1.32}$$

At the same time, in terms of the Lorentz tensor this model corresponds to the isotropic approximation $L_\parallel = L_\perp = 1/3$ in (1.6) and (1.7). On the contrary, in the model of Vuks the Lorentz tensor proves to be essentially anisotropic. We shall see below that the Vuks formula corresponds far better to the experimental data for real liquid crystals.

The physically most consistent model includes an anisotropic ellipsoidal Lorentz cavity that reflects the structural anisotropy of the LC. However, here the question arises of the degree of anisotropy of the cavity, which cannot be determined unambiguously within the framework of such a semiphenomenological approach. Different authors associate the anisotropy of the cavity with the geometric anisotropy of the molecule,[41] the optical anisotropy of the medium,[42,88] or the anisotropy of the correlation function.[36-38] The second question that arises in using an anisotropic Lorentz cavity consists in determining the mutual orientation of the cavity and the polarizability tensor of the molecule placed at its center. Evidently an answer to this question requires information on the correlations between the orientation of the molecule and the (microscopic) local field in the LC. In the simplest case we can assume that a molecule with a polarizability averaged over the orientations with account taken of the nematic order lies at the center of the effective spheroidal cavity, which is oriented along the optic axis of the nematic LC. Here the principal axis of the mean polarizability tensor lies along the axis of the cavity. When $S = 1$, the shape of the cavity corresponds to the shape of the molecular spheroid, whose semiaxis a and c can be found from the molecular model. In this case the field in the cavity is determined by the known formulas for a dielectric ellipsoid, which corresponds to the general expression (1.6) with $\mathrm{Sp}\,\hat{L} = 1$ and

$$L_\perp = \frac{1}{2e}\left(1 - \frac{1}{2em^2}\ln\frac{1+e}{1-e}\right). \tag{1.33}$$

For incomplete orientational order we have $S \neq 1$, and the shape of the cavity has a smaller anisotropy than the shape of the molecule, while the temperature variation of the anisotropy of the Lorentz tensor is approximated by a relationship[27] equivalent to (1.28):

$$\tau\,(T_c - T) = \frac{\tau_{\max}}{\Delta n_{\max}}\,\Delta n\cdot(T_c - T). \tag{1.34}$$

Here T_c is the temperature of the LC-isotropic liquid transition, $\tau_{\max} = (1/3) - L_\perp$, while the birefringence $\Delta n_{\max}$ of a fully ordered specimen is determined by the known relationship[60]

$$\Delta n = \Delta n_{\max}\cdot\left(1 - \frac{T}{T_1}\right)^\beta, \tag{1.35}$$

Here $T_1 > T_c$ and β are adjustment parameters. This model can also be interpreted within the framework of concepts of the effective local-field tensor (see above), whose axis are always oriented parallel to the axes of the tensor $\hat{\varepsilon}$, which coincide with the axes of the averaged polarizability tensor of the molecule. Here Eqs. (1.33) and (1.34) define a very simple model of the effective Lorentz tensor. We note also that the model of an anisotropic cavity effectively takes account of part of the long-range orientational correlations of the molecules. An equivalent method[29,42] of determining the semiaxes of the effective cavity when $S \neq 1$ is based on using x-ray data on the correlation functions in the liquid crystal.[61-63]

In the general case the principal axis of the molecular ellipsoid is oriented arbitrarily with respect to the optic axis of the LC. For such a system analytical expressions for the local field in the cavity were first derived by Segre[32] within the framework of the Onsager model. After averaging $\mathbf{E}_l$ over the molecular orientations for the nematic phase, expressions equivalent to (1.6) and (1.7) are obtained for the permittivity and the local-field tensor. Here the anisotropy of the effective Lorentz tensor is $\tau = \tau_{\max} S$ [which coincides with (1.28)].

Completely different variants of the answers to the questions posed above were chosen by de Jeu and Bordewijk,[41] who proposed that the cavity always has a constant anisotropy involving the shape anisotropy of the molecule, while the orientation of the axes of the local-field tensor is rigidly associated with the instantaneous orientation of the polarizability tensor of the molecule. In the model of Ref. 41 the local field in the cavity is also determined by the formulas for a dielectric spheroid, which are analogous to (1.33). However, the local field was understood to be the microscopic local field, whereas in the models of Refs. 27 and 42 it was the effective field.

Analysis of the model of de Jeu and Bordewijk from the standpoint of the molecular-statistical theory shows[22] that

the model is actually based on the hypothesis of complete correlation of the orientations of adjacent molecules of the LC. To obtain formally the results of Ref. 41, one must also assume that the orientations of adjacent molecules are correlated only if their centers of mass do not lie simultaneously inside a single molecular ellipsoid.[22] Evidently the latter follows from the mutual impenetrability of the molecules. However, actually the steric repulsion of two anisotropic particles defines the so-called excluded volume, which is not equal to the volume of the molecule, and which depends on their mutual orientation. It is also essential that the mean anisotropy of the excluded volume is not constant, but is approximately proportional to the order parameter S.

We note that an analogous hypothesis of complete correlation between the orientation of the molecule and the local field is used also in the model of Petrov and Derzhanskiĭ. However, in the latter model the anisotropy of the ellipsoidal cavity is determined by the anisotropy of the LC.[88]

A common feature of all the models that employ an ellipsoidal Lorentz cavity is that they do not take sufficient account of the intermolecular correlations (primarily the short-range ones) in the LC. Actually the field created by the anisotropic molecules at the center of the anisotropic cavity generally does not equal zero, and it contributes to the overall susceptibility. Strictly speaking, even a spherical Lorentz model yields a result that coincides with the result of the microscopical calculation only in the case of a cubic lattice. Even in an isotropic liquid a fluctuating field arises at the center of the cavity that involves the thermal motion of the molecules. In the case of a liquid crystal, along with the translational fluctuations, also strong orientational fluctuations exist, which play a large role in anisotropic liquids. Therefore it is difficult to estimate from general considerations the accuracy of the results obtained within the framework of the ellipsoidal-cavity model; the decisive argument here is comparison with experiment. At the same time one can state that the polarizability of a molecule found within the framework of the cavity model should not be identified with the polarizability of an isolated molecule, e.g., in the gas phase. It is more consistent to assume that a molecule lies at the center of the cavity having an effective polarizability renormalized owing to the interaction and correlations with the closest neighbors.

Another approach to the problem of the local field in a liquid crystal consists in using lattice models, the simplest of which amounts to a tetragonal lattice with one molecule per unit cell.[21] In the point-polarizability approximation the tensor $\hat{\Phi}$ has the form of (1.6), with $\tau < 0$ for extended molecules, and with $|\tau|$ rapidly increasing with increasing axial ration m. Even at $m_0 = 1.4$ the component $L_{\parallel}$ changes sign,[21] and the real values of the anisotropy of the molecules of the LC correspond to strongly elevated values of τ. This overestimate of the role of the structural anisotropy of the LC arises from not taking account of the distribution of the polarizability throughout the volume of the molecule and of the translational fluctuations of the molecules. The most popular model based on the lattice theory is that of Neugebauer,[34] in which the relation of the components ε_α and γ_α is formally reduced to Eqs. (1.6) and (1.7) with account taken of $\mathrm{Sp}\hat{L} = 1$. However, the extension of lattice models to the case of a liquid crystal leaves indeterminate the choice of the symmetry group and the lattice parameters. In the Neugebauer model this difficulty is avoided[35] by using the assumption that the Lorenz-Lorentz formula is valid in the isotropic phase of the LC, and that the mean polarizability of the molecules is constant in going from the isotropic to the nematic phase. The latter assumption would be justified if the polarizability of the isolated molecule were used in the model. However, as was noted above, it is more consistent to assume that in the studied models the polarizability $\hat{\gamma}$ is the effective quantity renormalized owing to the short-range interactions. This conclusion corresponds to the empirical relationship (1.14), in which we have[27,42]

$$\frac{\bar{\varepsilon}-1}{\varepsilon+2} = \frac{4\pi N}{3}\bar{\gamma}\left(1 + \frac{3\Delta\varepsilon\cdot\tau}{\bar{\varepsilon}+2} + \frac{2S\Delta\gamma\cdot\Delta f}{3\bar{\gamma}(\bar{\varepsilon}+2)}\right). \tag{1.36}$$

We see from (1.36) that fulfillment of the relationship (1.14) does not ensure the constancy of $\bar{\gamma}$, but the constancy of the product $\bar{\gamma}[\ldots]$. Yet if we assume that the quantity $\bar{\gamma}$ is constant, then, within the framework of the Neugebauer model, Eqs. (1.14), (1.36), and (1.25) imply a severe restriction on the sign of the anisotropy of the local field

$$\Delta f > 0, \quad |\tau| < |\tau_k| \tag{1.37}$$

for all liquid crystals independently of their electronic structure and spectral region of study. A number of other features of the Neugebauer model have been treated in Ref. 71.

The relation between the cavity model and the lattice models of LCs is of interest. As we have already noted above, the local field of a spherical Lorentz cavity coincides with the local field calculated exactly for a cubic lattice of point dipoles. Recently analogous studies were performed also for the case of anisotropic media. In Ref. 33 the local field was calculated in a molecular crystal having one molecule in a hexagonal unit cell by using the model of an ellipsoidal cavity. The results were compared with the exact calculations within the framework of the lattice theory.[15] Here, to take account of the shape of the molecule and the polarizability distribution in the microscopical calculation, a molecule having the axial ratio m was modeled in the form of m fragments lying along its axis. We note that the tensor $\hat{L}$ for a molecule is obtained as a result of averaging the submolecu-

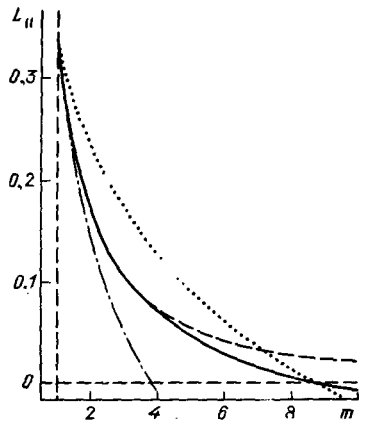

FIG. 1. Dependences of the component $L_{\parallel}$ of the Lorentz tensor on the axial ratio m of the dimensions of the molecule as calculated for a crystal with one molecule in a hexagonal unit cell within the framework of the statistical theory (solid line)[33] and of the continuum theory by (1.32) (dashed line), for a nematic LC with $S = 1$ by (1.43) (dot-dash line), and by (1.44) (dotted line).

lar tensor $\hat{L}_k$,[15,33] and it has a smaller anisotropy than in the point-polarizability approximation. As we see from Fig. 1, for typical mesogenic molecules with $m \lesssim 5$, the results of the statistical and the continuum theories coincide. This can serve as an argument in favor of the applicability of the cavity model for calculating the dielectric properties of LCs for $S \approx 1$. Comparison with the results noted above[21] shows that taking account of the nonlocality of the polarizability within the framework of the microscopical calculation leads to rapid increase in the parameter $m_0 = m(L_\parallel = 0)$. It is natural to assume that, when $S \neq 1$ in the LC, the model of an effective ellipsoidal Lorentz cavity is adequate for fixing the molecule in a lattice having the same spatial anisotropy, while the shape of the cavity must reflect the anisotropy of the radial distribution function of the molecules.[27,36,42] Yet it remains unclear to what degree the correspondence of these two approaches is preserved upon taking account of the translational and orientational fluctuations in real liquid crystals.

1.4. Taking account of intermolecular correlations

The first attempt to take *explicit account* of the correlations of the molecules was undertaken in Refs. 36 and 37, in which a statistical approach was used jointly with the Lorentz approach. The aim of Ref. 36 was to construct a form of the cavity in the LC that would ensure the vanishing (on the average) of the field at its center arising from the rest of the molecules within the cavity. However, this problem cannot be solved exactly, and the corresponding result was obtained[36] only within the framework of a simplified model that did not take account of the orientational fluctuations of the anisotropic polarizability of the molecules, while all the quantities were subjected to a prior averaging with respect to orientations. Consequently the orientational correlations and the correlations between the position and orientation of a molecule, which play an important role in LCs owing to the rather dense packing of the anisotropic molecules, also were not taken into account. With allowance for the approximations made, the mean field at the center of the cavity is written in the form

$$E_\alpha = N\mu_\beta \int \mathrm{d}\mathbf{u} \int_* \mathrm{d}r g_2(\mathbf{r})(3u_\alpha u_\beta - \delta_{\alpha\beta}) r^{-1}, \qquad (1.37')$$

Here $g_2(\mathbf{r})$ is the anisotropy of the pairwise correlation function, μ is the mean induced dipole of the molecule, $\mathbf{u} = \mathbf{r}/r$, while the integration over r in (1.37) is performed within the limits of the cavity, as defined by the equation ($r = kF(\mathbf{u})$, where the explicit form of the function $F(u)$ is found in Ref. 36. Thus having eliminated the contribution of the molecules within the cavity, the local field created by the molecules outside the cavity can be found in the continuum limit, since the dimensions of the cavity can be made sufficiently large. Consequently the expression for the local-field tensor also has the form (1.6), where $L_\alpha = (1/3) + \eta_\alpha$,

$$\eta_\alpha = -(4\pi)^{-1} \int \ln F(\bar{\mathbf{u}})(3u_\alpha^2 - 1)\,\mathrm{d}\mathbf{u}, \qquad (1.38)$$

Here we have $\mathrm{Sp}L = 1$. Upon taking account of the steric correlations between the rigid ellipsoids in Ref. 38, the following expression was obtained for the parameters η_α apart from quadratic terms in S:

$$\eta_\parallel = -\frac{4}{5}\frac{m-1}{m+2} S + \frac{8}{35}\left(\frac{m-1}{m+2}\right)^2 S^2. \qquad (1.39)$$

When $S = 1$, Eq. (1.39) implies that $L_\parallel < 0$ when $m > 3.8$. Comparison with the results of the previous section and Fig. 1 shows that the model being studied occupies an intermediate position between the two lattice models,[21,33] one of which takes account of the nonlocality of the molecular polarizability, while the other neglects it. Here taking account of the statistics of the translational distribution of the molecules reduces the anisotropy of the tensor, but to a far smaller degree than when one takes account of the nonlocality of the polarizability.

References 22, 72, and 73 developed different approaches to the molecular-statistical description of the optical properties of LCs within the framework of the point-polarizability model. However, here various simplifying assumptions were made that did not allow obtained sufficiently general results. For example, in Ref. 73 the final expressions were derived without taking account of the orientational correlations between the molecules of the LC. We note that a rather consistent treatment was conducted in Ref. 72. However, its generality was restricted by the assumption of independence of the correlation functions of the orientation of the molecules. Here Ref. 72 actually contains a simplified variant of the consistent statistical theory published earlier.[23,24]

In Ref. 22 a theory was constructed of the refractive indices of nematic LCs with account taken only of the pairwise steric correlations. Here the components of the effective Lorentz tensor have the form

$$L_\parallel = \frac{1}{3} - 2w + 2w\frac{(1-\varkappa)(1-S)}{1+2\varkappa S},$$
$$L_\perp = \frac{1}{3} + w - w\frac{(1+2\varkappa)(1-S)}{1-\varkappa S}, \qquad (1.40)$$

Here we have $\varkappa = \Delta\bar{\gamma}/3\gamma$, while the parameter $w = (2/45)\ln[m(m+1)/2]$ characterizes the shape of the molecule. When $S = 0$ we have $L_\parallel = L_\perp < 1/3$ and $\mathrm{Sp}L = 1 - 6w\varkappa$. In the mesophase we find $L_\perp > L_\parallel$ and for typical values $\kappa \approx 0.3$, we have $\tau \sim S$ to high accuracy. When $S = 1$, then we have $\mathrm{Sp}\hat{L} = 1$, and the model being discussed is formally equivalent to the models discussed above of the effective local field. As we see from Fig. 1, as m increases, one observes a sign change of $L_\parallel$ characteristic of the point-dipole approximation, which points out the need to take account of the nonlocality of the polarizability. We can neglect the weak $L(\lambda)$ dependence throughout the region of optical transparency of the LC.[58]

A consistent molecular-statistical theory of the high-frequency permittivity of LCs was developed recently.[23,25] However, here rigorous results as yet have been obtained only in the dipole approximation within the framework of the point-polarizability model. Within the framework of this model one can construct formally exact expressions for the refractive indices of LCs with account taken of multiparticle correlations, which are then used to obtain concrete approximate formulas for different phases of the LC, and also to elucidate the physical meaning of the approximations that the various semiphenomenological theories are actually based on. Below we shall examine the fundamental concepts and results of this theory, which was developed by analogy

with the theory of anisotropic liquids.

In a condensed molecular medium one can determine the microscopic polarization $\mathbf{p}^{m}(\mathbf{r},t)$, which is determined by the dipole induced in the molecules of the medium at the given point r:

$$\mathbf{P}^{M}(\mathbf{r},t)=\sum_{i}\mathbf{p}_{i}\delta(\mathbf{r}-\mathbf{r}_{i}(t)), \tag{1.41}$$

Here $\mathbf{p}_i$ is the dipole of the molecule i. The microscopic polarizability is related to the microscopic electric field $\mathbf{E}^{m}$ in a nonmagnetic medium by the following known equation:

$$\operatorname{rot}\operatorname{rot}\mathbf{E}^{M}+\frac{1}{c^{2}}\frac{\partial^{2}\mathbf{E}^{M}}{\partial t^{2}}=-\frac{1}{c^{2}}\frac{\partial^{2}\mathbf{p}^{M}}{\partial t^{2}}, \tag{1.42}$$

whose general solution can be written in operator form:

$$\mathbf{E}^{M}=\mathbf{E}_{0}-\int\hat{F}(\mathbf{r}-\mathbf{r}',\omega)\,\mathbf{P}^{M}(\mathbf{r}',\omega)\,d\mathbf{r}', \tag{1.43}$$

Here $\mathbf{E}_0$ is the external field, while the operator $\hat{F}(\mathbf{R},\omega)$ has the form

$$\hat{F}(\mathbf{R},\omega)=\frac{4\pi}{3}\delta(\mathbf{R})+\left[\left(1+\frac{i\omega R}{c}-\frac{\omega^{2}R^{2}}{3c^{2}}\right)(1-3\mathbf{uu})-\frac{2\omega^{2}R^{2}}{3c^{2}}\right]e^{iR\omega/c}R^{-3}. \tag{1.44}$$

Within the framework of the molecular optics of liquid crystals, the quantity $\mathbf{R}=\mathbf{r}-\mathbf{r}'$ is practically restricted to the correlation radius ξ, which is always smaller than the wavelength of light ($\xi\ll\lambda$). Therefore we have $\omega R/c\ll 1$, and the operator $\hat{F}(\mathbf{R},\omega)$ in the optical range acquires the simple form of a dipole-dipole interaction operator:

$$\hat{F}(\mathbf{R},\omega)\approx\frac{4\pi}{3}\delta(R)+R^{-3}(1-3\mathbf{uu}),\quad R\ll\lambda. \tag{1.45}$$

The dipole moment $\mathbf{p}_i$ of the molecule is induced by the macroscopic local field $\mathbf{E}_L(\mathbf{r}_i)$ created by all the rest of the dipoles induced in the other molecules of the medium:

$$\mathbf{P}_{i}=\hat{\alpha}(\theta_{i},\omega)\,\mathbf{E}_{L}(\mathbf{r}_{i},\omega), \tag{1.46}$$

$$\mathbf{E}_{L}(\mathbf{r}_{i},\omega)=\mathbf{E}_{0}-\sum_{i\neq j}\hat{F}(\mathbf{r}_{i}-\mathbf{r}_{j},\omega)\,\mathbf{p}_{j}-\frac{1}{2}(\hat{F}-\hat{F}^{+})\,\mathbf{p}_{i}, \tag{1.47}$$

Here $\hat{F}^{+}$ is the operator conjugate to $\hat{F}$. The third term in (1.47) is defined as the so-called self-interaction of the molecule i, which in the nonrelativistic case is reduced to radiation friction.

As was shown in Refs. 23 and 24, one can use Eqs. (1.43)–(1.47) to obtain a closed equation for the microscopic polarization:

$$\mathbf{P}_{M}(\mathbf{r},\omega)=\hat{\gamma}^{*}(\theta)\left[\mathbf{E}_{0}-\int\hat{H}(\mathbf{r}-\mathbf{r}',\omega)\,\mathbf{P}_{M}(\mathbf{r}',\omega)\,d\mathbf{r}'\right], \tag{1.48}$$

where we have

$$\hat{\gamma}^{*}=\int\hat{\gamma}(\theta)\,\rho(r,\theta,t)\,d\theta, \tag{1.49}$$

and the quantity ρ amounts to the microscopic density of number of particles in the phase space (r,θ):

$$\rho(\mathbf{r},\theta,t)=\sum_{i}\delta(\mathbf{r}-\mathbf{r}_{i}(t))\,\delta(\theta-\theta_{i}(t)), \tag{1.50}$$

Here we find that the operator $\hat{H}=\hat{F}$ when $|\mathbf{r}-\mathbf{r}'|\geqslant D$ and $\hat{H}=(\hat{F}+F^{+})/2$ when $|\mathbf{r}-\mathbf{r}'|<D$.

The macroscopic permittivity of the liquid crystal $\chi=(\varepsilon-1)/4\pi$ relates the macroscopic polarization $P=\langle P_M\rangle$ and the field $\mathbf{E}=\langle E_M\rangle$ in the medium; $\langle\ldots\rangle$ denotes averaging over the ensemble. By using Eqs. (1.48) and (1.43) one can obtain a formally exact expression for the permittivity of the liquid crystal within the framework of the adopted model:

$$(\hat{\varepsilon}-1)(\hat{\varepsilon}+2)^{-1}=\frac{4\pi}{3}\hat{\beta}, \tag{1.51}$$

$$\hat{\beta}=\langle\hat{\gamma}^{*}(1+\hat{H}\hat{\gamma}^{*})^{-1}\rangle\,\langle(1+\hat{H}\hat{\gamma}^{*})^{-1}\rangle^{-1}. \tag{1.52}$$

Thus the general expression for the high-frequency permittivity of the LC in the dipole approximation has the form of a generalized Clausius-Mossotti relationship, in which, instead of the polarizability of the individual molecule, the effective quantity $\hat{\beta}$ appears. The latter is the renormalized polarizability with account taken of the interaction with the rest of the molecules and of the intermolecular correlations. We note that Eq. (1.52) amounts to a generalization of the corresponding formula for an isotropic liquid consisting of isotropic molecules.

In Eq. (1.52) the fluctuating quantity is the polarizability $\hat{\gamma}^{*}$, which depends on the microscopic density ρ. One can expand the renormalized polarizability $\hat{\beta}$ in a power series in the fluctuation of the polarizability $\Delta\hat{\gamma}^{*}$:

$$\hat{\beta}=\rho_{0}\hat{\gamma}-\rho_{0}^{2}(2\pi)^{-3}\int d\mathbf{k}'\,d\theta\,d\theta' g_{2}(\mathbf{k}-\mathbf{k}',\theta,\theta')\times\hat{\gamma}(\theta)\,\hat{K}(\mathbf{k}',\omega)\,\hat{\gamma}'(\theta')+\ldots, \tag{1.53}$$

Here $\hat{K}=(1+\rho_0\hat{H}\hat{\gamma})^{-1}\hat{H}$, $\hat{\gamma}$ is the mean polarizability of the molecule as determined by the general formulas (1.8), and $g_2(\mathbf{k},\mathbf{k}',\theta,\theta')$ is the pairwise correlation function of the liquid crystal. The subsequent terms of the expansion (1.53) are determined by the higher-order correlation functions. We can assume that the correlation corrections of higher order make a rather small contribution to the effective polarizability owing to the weakening of the multiparticle correlations and the relative smallness of parameter $\rho_0\gamma$ in which the expansion is being performed [$\rho_0\gamma\sim 10^{-1}$ for real LCs]. This assumption is confirmed also in the theory of isotropic liquids, where it has been shown that expressions of the type of (1.53) in which only the pairwise correlations are taken into account describe very well the relation between the polarizability of the molecules and the refractive index of a large number of simple liquids.

By using the renormalized polarizability $\hat{\beta}$ we can also write general expressions for the effective local field and the Lorentz tensor, which in the case of nematic liquid crystals have the simple form:[23]

$$f_{\parallel}=\frac{n_{\parallel}^{2}+2}{3}\left(1+\frac{\varkappa_{\parallel}}{\gamma_{\parallel}}\right),\quad f_{\perp}=\frac{n_{\perp}^{2}+2}{3}\left(1+\frac{\varkappa_{\perp}}{\gamma_{\perp}}\right), \tag{1.54}$$

$$L_{\parallel}^{\mathrm{eff}}=\frac{1}{3}+\frac{\varkappa_{\parallel}}{4\pi\rho_{0}\gamma_{\parallel}\beta_{\parallel}},\quad L_{\perp}^{\mathrm{eff}}=\frac{1}{3}+\frac{\varkappa_{\perp}}{4\pi\rho_{0}\gamma_{\perp}\beta_{\perp}}, \tag{1.55}$$

Here $\varkappa_{\parallel}$ and $\varkappa_{\perp}$ are the correlation corrections to the renormalized polarizability $\varkappa_k=\beta_k-\rho_0\gamma_k\,(k=\perp,\parallel)$.

The expressions (1.53)–(1.55) are rather general, so

that concrete formulas can be derived with the aid of these expressions using various approximations. In particular, one can define approximations on which a number of the semi-phenomenological theories discussed above are actually based, and also elucidate their physical meaning.[70,71] The simplest formulas for the refractive indices are derived in the molecular-field approximation, in which one neglects all the correlation corrections. In this case we have $\hat{\beta} = N\hat{\gamma}$, and Eqs. (1.51) and (1.52) go over into the generalized Clausius-Mossotti formula [cf. (1.32)], which was discussed above. Thus the zero-order approximation of this theory corresponds to the Lorentz theory. At the same time, the generalized Clausius-Mossotti formulas can hardly be used for calculating the parameters of thermotropic LCs, since the neglect of the correlations,which play an important role in such systems, can lead to considerable errors.[71] We note also that, in line with the formulas of (1.55), the anisotropy of the effective Lorentz tensor is fully determined by the intermolecular correlations. The first and the subsequent approximations in the expansion in (1.53) correspond to taking account of the contribution of binary, ternary, etc., intermolecular correlations in the formation of the local field in the liquid crystal. Here the first correlation correction, as a rule, plays a substantial role, since the expansion parameter $\rho_0\gamma$ is insufficiently small.

One can derive more exact expressions for the refractive indices of liquid crystals only if one has sufficiently detailed information on the pairwise correlation function of the LC $g_2(\mathbf{r}_{12}, \theta_1, \theta_2)$ that enters into (1.53). However, at present only the behavior of $g_{12}(1,2)$ at small intermolecular distances, where it is determined by the excluded volume effect, and at large distances, where the correlations are governed by the energy of the dispersion interaction, is well known. Upon taking account of these properties of the correlation function in liquid crystals, the following expressions were derived[25] for the refractive indices of the nematic phase:

$$\frac{n_\parallel^2-1}{n_\parallel^2+2} = \frac{4\pi}{3}N\beta_\parallel = \frac{4\pi}{3}N\left\{\bar{\gamma} + \frac{2}{3}S\Delta\gamma + N\nu_2\left[S\bar{\gamma}^2 - \frac{1}{3}(S^2 - S + 2)\Delta\gamma\bar{\gamma} + \frac{1}{9}S(2-S)(\Delta\gamma)^2\right]\right\}, \tag{1.56a}$$

$$\frac{n_\perp^2-1}{n_\perp^2+2} = \frac{4\pi}{3}N\beta_\perp = \frac{4\pi}{3}N\left\{\bar{\gamma} - \frac{1}{3}S\Delta\gamma + N\nu_2\left[3S\bar{\gamma}^2 + S(1+S)\Delta\gamma\bar{\gamma} + \frac{1}{3}S(S+2)(\Delta\gamma)^2\right]\right\}, \tag{1.56b}$$

$$\nu_{2a} = \frac{16\pi}{15}\left(\ln\frac{L+D}{2D} - G_2\right) = \nu_{2S} - \nu_{2a}. \tag{1.57}$$

The corresponding expressions for the effective-field tensors and the effective Lorentz tensor can be derived by using the general formulas (1.6) and (1.7) by substituting Eqs. (1.54) and (1.55) into them.

The components of the effective polarizability $\beta_\parallel$ and $\beta_\perp$ in (1.56) substantially depend on the correlation parameter ν_2, which amounts to the difference between two quantities. One of them is determined by the short-range steric correlations and depends only on the geometric parameters of the molecules,whereas the second term $\nu_{2a} = 16\pi\ G_2/15$ contains the unknown parameter G_2, which characterizes the correlations of molecules not in contact, mainly involving their attraction. Thus the magnitude of the correlation correction is determined by the balance of attractive and repulsive forces of the molecules, as is characteristic also for describing other properties of LCs, including the onset of orientational order itself.

Analogously one can derive expressions for the refractive indices of a biaxial smectic C phase[24] in which the director $\mathbf{n}$ is inclined by the angle θ to the smectic layers formed by the molecules of the liquid crystal. At small angles of inclination $\theta^2 \ll 1$ we have

$$\frac{n_z^2-1}{n_z^2+2} = \frac{4\pi}{3}N\left\{\gamma_\parallel - N(1-\sigma)\nu_2\left[2\gamma_\parallel^2\left(1 - 3\sin^2\frac{\theta}{4}\right) + \Delta\gamma\gamma_\perp\right]\right\}, \tag{1.58a}$$

$$\frac{n_x^2-1}{n_x^2+2} = \frac{4\pi}{3}N\gamma_\perp[1 + N\gamma_\perp(1-\sigma)\nu_2(1 - 3\sin^2\theta)], \tag{1.58b}$$

$$\frac{n_y^2-1}{n_y^2+2} = \frac{4\pi}{3}N\gamma_\perp[1 + N\gamma_\perp(1-\sigma)\nu_2], \tag{1.58c}$$

Here σ is the fraction of the nearest neighbors of a molecule lying in the same smectic layer with it. The $\mathbf{z}$ axis is directed perpendicular to the smectic layers, while the y axis lies in the plane of the layers perpendicular to the director. A smectic A phase has the angle $\theta = 0$, and the principal refractive indices are $n_\parallel = n_z$ and $n_\perp = n_x = n_y$ for $\theta = 0$.

The refractive indices in smectic A and C phases were measured in Refs. 77 and 150 for two homologous series of liquid crystals. In particular, it was found that, in going from the A to the C phase, the refractive index n_y is a "continuation" of the index $n_\perp$, the authors of Refs. 77 and 150 having found no explanation for this. However, this result can be easily explained by using Eqs. (1.58), since the refractive index n_y does not depend on the angle θ, and $n_y = n_\perp$. The expressions of (1.58) imply that the difference n_x must increase linearly with the temperature for small deviations from the A–C transition point since, when $\theta^2 \ll 1$, we have $n_x - n_y \sim \theta^2 \sim T_{AC} - T$. Moreover, we see from Eq. (1.58a) that a jump in the derivative $\partial n_z/\partial T$ must occur at the A–C transition point. We note that all the listed features of the temperature dependence of the refractive indices of a C smectic actually have been observed experimentally.

The theory of the optical properties of liquid-crystalline mixtures and doped LCs has been developed in Refs. 58 and 78–81. Here Refs. 79 and 80 employed the isotropic approximation (1.22) for the molecules of the matrix and the dopant. For mixtures of LCs, the difference between the effective fields acting on molecules of different types α is taken into account by the difference in effective Lorentz tensors, while the effective tensor $\hat{f}_\alpha$ has the form[78,81]

$$f_{\alpha j} = 1 + L_{\alpha j}(\varepsilon_j - 1), \tag{1.59}$$

Here $\hat{\varepsilon}$ is the high-frequency permittivity tensor of the mixture, which is given by the expression

$$\varepsilon_j - 1 = 4\pi N\sum_\alpha x_\alpha\gamma_{\alpha j}f_{\alpha j}, \tag{1.60}$$

$x_\alpha = N_\alpha/N$ is the molecular concentration of the compo-

nent α, while the components are given by Eq. (1.8). On the basis of these general considerations and a number of additional assumptions, one can explain[58,78,81] the empirical rules of additivity of the molecular refractions (1.14)[82–85] and more complicated combinations of the parameters $\varepsilon_{\alpha j}^{2}$[86,87] and indicate their conditions of applicability.

The molecular-statistical theory of the high-frequency permittivity of a liquid crystal[81] as a whole can be constructed by analogy with the one-component case. Here one must take account of the fact that the molecules of the different components have different polarizabilities $\hat{\gamma}_\alpha$ and that different microscopic local fields act on them. As a result one obtains the following general expressions for the refractive indices of a multicomponent nematic liquid crystal:[81]

$$\frac{n_k^2-1}{n_k^2+2}=\frac{4\pi}{3}N\beta_k=\frac{4\pi}{3}N\left(\sum_\alpha x_\alpha\gamma_{\alpha k}-N\sum_{\alpha,\delta}x_\alpha x_\delta\lambda_{\alpha\delta k}+\ldots\right), \tag{1.61}$$

$$\lambda_{\alpha\delta k}=\int g_{\alpha\delta}(\mathbf{R}-\mathbf{R}',\theta,\theta')\,\hat{\gamma}_\alpha(\theta)\,\hat{K}(\mathbf{R}-\mathbf{R}',\omega)\times\hat{\gamma}_\delta(\theta')\,d\mathbf{R}\,d\theta\,d\theta'\quad(k=\parallel,\perp), \tag{1.62}$$

Here the $g_{\alpha\delta}$ are the pairwise correlation functions for the molecules of the components α and δ.

In line with the formulas of (1.6), the refractive indices of mixtures of LCs must have a nonlinear dependence on the concentration of the components. Here we must distinguish two cases. In the first case the molecules of the different components differ weakly from one another and one can approximately assume that $\lambda_{\alpha\delta}\simeq(\lambda_{\alpha\alpha}+\lambda_{\delta\delta})/2$. Then the concentration dependence in (1.61) becomes linear, and Eq. (1.61) implies an additivity rule of the refractions, which has been established empirically for a number of LCs. We can expect that this rule will also be fulfilled for the most varied mixtures of nonpolar LCs, since in such mixtures the deviations from a linear concentration dependence of the different parameters are generally small. At the same time, in a mixture of weakly and strongly polar molecules, the corresponding dependences are substantially nonadditive. This involves the strong dipole-dipole correlations, including the forming of the diameters. For such mixtures the additivity of the refractions must appreciably break down, and we can no longer represent the quantity $\hat{\beta}$ as a weighted sum of the effective polarizabilities.

By using the formulas of (1.61) one can also obtain expressions for the components of the effective local-field tensor and the Lorentz tensor of a mixture of nematic liquid crystals:[81]

$$f_{\alpha k}=\frac{n_k^2+2}{3}\left[1-N\sum_\delta x_\delta\lambda_{\alpha\delta k}(\gamma_{\alpha k})^{-1}\right],$$
$$L_{\alpha k}=\frac{1}{3}-N\sum_\delta x_\delta\lambda_{\alpha\delta k}\frac{1}{4\pi\gamma_{\alpha k}\beta_k}. \tag{1.63}$$

The equations of (1.63) imply that the effective local fields acting on the molecules of the different components generally must differ. This difference is manifested most graphically in the case of a liquid crystal with a dopant for which $x_1=x_d\simeq 0$, $x_2=x_m\simeq 1$: the local field acting on a molecule of the dopant is determined by the correlations between the molecules of the dopant and of the matrix of the LC, while the field acting on a molecule of the matrix is determined by the correlations only between the molecules of the matrix. If the structure and the dimensions of the molecules of the dopant and of the matrix differ appreciably, then also the corresponding effective fields must differ. However, we must note that the existing experimental data[58] indicate a weak dependence of the effective local field on the type of dopant. The reason for this disagreement as yet remains unclear, and we can only assume that this case manifests a defect of the theory involving neglect of the distribution of polarizability throughout the volume of the molecule.

1.5. Of what does the problem of the local field in liquid crystals consist?

Analysis of the different approaches to the theoretical description of the local field in liquid crystals has shown that, despite the considerable advances achieved in recent years in constructing a consistent molecular-statistical theory of the optical properties of LCs, the level of development of the theory as yet does not enable quantitative calculations of the parameters of the effective local field for concrete systems. The latter involves the simplifications on which the theory is based (primarily the lack of taking account of the distribution of polarizability throughout the molecular volume) and the insufficient information on the short-range correlations in LCs. Therefore, from the practical standpoint, certain simple models of the local field retain great significance and do not contradict the fundamental qualitative conclusions of the statistical theory.

From the standpoint of analyzing the experimental data, an adequate model of the tensor $\hat{f}$ must satisfy the following requirements:[58] 1) The form of $\hat{f}$ should be the same for all methods of molecular optics and spectroscopy, independently of the spectral region. 2) The results of determining the characteristics of the structural order of the molecules throughout the region of the mesophase by different optical and spectral methods must agree among themselves and with the results of independent physical measurements (NMR, x-ray diffraction, magnetometry, etc.) that do not require taking account of the corrections to the local field. 3) The results of determining the molecular parameters must agree with the spatial, chemical, and electronic structure of the molecules in the different spectral regions.

We note that these requirements presuppose the existence of dispersion, as well as a dependence of the effective local field on the chemical and electronic structure of the molecules. Thus the problem of the local field in liquid crystals is reduced to the following problems: establishment of the relation of the measurable optical and spectral parameters of the liquid crystal to the anisotropy of the tensor $\hat{f}$ of (1.8); the theoretical or experimental determination of $\hat{L}$; the determination of the structural and molecular parameters of liquid crystals from optical measurements with verification of fulfillment of the requirements 2) and 3) indicated above. Realization of this program enables us to proceed from noting the variety of models of the local field and the difficulties of quantitative interpretation of the optical experiments[1,76,88,90] to analyzing objectively the degree of adequacy of these models, to explaining the effects corresponding to them, and to elucidating the possibilities of experimental solution of the problem of the local field in liquid crystals.

2. EFFECTS OF THE LOCAL FIELD IN THE MOLECULAR OPTICS OF LIQUID CRYSTALS

The anisotropy of Δf of (1.24) is proportional to the long-range orientational order parameter of the LC. Consequently it makes a contribution to the anisotropy of all the optical properties of the LC, which contains a leading term linear in Δf. Therefore the corrections for the anisotropy of the LF to the experimentally determinable molecular and structural parameters of the LC also begin with terms linear in Δf, while one can decide on the degree of applicability of some particular model of calculating $\hat{L}$ already from the sign of Δf in this model, having taken as the zero-order approximation $\Delta f = 0$ and upon comparing the values of the structural and molecular parameters corresponding to it with those measured by independent methods.

2.1. Refractometry

The Lorenz-Lorentz formula (1.16) is valid for an isotropic liquid having isotropic molecules. For anisotropic molecules, taking account of the intermolecular correlations leads to the appearance on the right-hand side of (1.16) of correlation corrections that depend on the anisotropy of the molecular shape and on $\Delta\gamma$.[16,22,72,91] However, experiment[92] shows that (1.16) is fulfilled with high accuracy, both for isotropic and for strongly anisotropic molecules of rod- and disk-shaped form. This indicates the actual smallness of the correlation corrections and serves empirically to substantiate the applicability of (1.16) to the isotropic phase of LCs (see also (1.13)–(1.15)). Comparison of (1.36) with (1.14) and (1.28) shows that, when $\Delta f \leqslant 0$, the isotropic liquid-nematic LC (I-N) phase transition and the increase in S are accompanied by an increase in $\bar{\gamma}$. This agrees with the theoretical[18,20,92,93] and experimental[15,94,95] facts of increase in $\bar{\gamma}$ owing to renormalization of the polarizability caused by the intermolecular interaction.

If one has absolute values of S known from independent measurements, one can use Eqs. (1.7)–(1.9) to determine γ.[59,60,64–70,104,105] Here the result substantially depends on taking account of the anisotropy Δf.[40,43,88,89] For uniaxial molecules the relationship is fulfilled that[27,58]

$$S\Delta\gamma = \frac{\Delta\varepsilon}{4\pi N\bar{f}}\left[1 + \frac{\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)^2}{3\bar{f}}\left(\frac{\tau}{\tau_k} - 1\right)\right]$$

$$\equiv \frac{\Delta\varepsilon}{4\pi N\bar{f}}(1 + \sigma), \tag{2.1}$$

Here the parameter σ has the meaning of a correction for the local field to the value of S determined from refractometric data. Upon taking account of (1.14), (1.21), (1.27) and the fact that $\Delta\varepsilon \ll 3(\bar{\varepsilon} - 1)$, we see from this that the fundamental contribution to σ comes from the term independent of S, while $\sigma \gtrless 0$ when $\Delta f \lessgtr 0$, or $|\tau| \gtrless |\tau_k|$. Equation (2.1) implies a quite definite relationship between the values of the anisotropy of the molecular polarizability $\Delta\gamma$ calculated by using the set of models discussed above:

$$\Delta\gamma_{\rm PM} < \Delta\gamma_{\rm V} < \Delta\gamma_{\rm ASh}. \tag{2.2}$$

Here the subscripts PM and V pertain, respectively, to the models of Palffy-Muhoray[36–38] and Vuks,[31] and the subscript ASh to the model proposed in Ref. 27. In the Vuks and Palffy-Muhoray models the value of $\bar{\gamma}$ in (1.16) is the same, and we obtain from (1.36) and (2.2) the following relationships of the components of the polarizability:

$$\gamma_i^{\rm PM} < \gamma_i^{\rm V} < \gamma_i^{\rm ASh},$$
$$\gamma_i^{\rm ASh} < \gamma_i^{\rm V} < \gamma_i^{\rm PM}. \tag{2.3}$$

These inequalities are general consequences of the assumptions on which the determination of the components $L_{\parallel,\perp}$ is based in the corresponding models of the local field. They do not depend on the properties of the concrete objects, and are confirmed by all known results of studying uniaxial liquid crystals.

One can decide on the correctness of any model of the local field within the framework of refractometry on the basis of comparing the values of $\Delta\gamma$ found by using (2.1) with the same quantities measured by independent methods in the isotropic phase of the LC or in an isotropic solution. For example, for 5CB the value $\Delta\gamma = 26.5$ Å^3 ($\lambda = 589$ nm) found by extrapolation to $T = T_c$ of the $\Delta\gamma(\Delta T)$ relationship[89] calculated by Eqs. (1.33)–(1.35) and (2.1) agrees with the value $\Delta\gamma = 27$ Å^3 found from data on the optical Kerr effect in the isotropic phase of 5CB.[96] The closeness of the value $\Delta\gamma = 23.6$ Å^3 ($\lambda = 633$ nm) found for MBBA by Eqs. (1.22) and (2.1) in the approximation $\sigma = 0$[26] to the value $\Delta\gamma = 27.4$ Å^3 measured[97] by the light-scattering method in an isotropic solution indicates a small anisotropy $\Delta f < 0$ for MBBA in this region of the spectrum, as is also confirmed by calculation by (1.29)[40] and by experiment.[43]

When the values of $\Delta\gamma$ are known from independent measurements, one can determine by Eq. (2.1) the absolute values of S from refractometric data. For fixed $\Delta\gamma$ and $\sigma \gtrless 0$, Eq. (2.1) implies that $S \gtrless S_i$, where $S_i = S(\sigma = 0)$. A weak $\sigma(\Delta T)$ dependence leads to similar temperature dependences of S and $S_i(T)$.[53,98] For all uniaxial liquid crystals studied up to now in the visible region of the spectrum we find $\Delta f < 0$ and $\sigma < 0$. Therefore, for fixed $\Delta\gamma$ for the local-field models discussed above, the following inequalities should be fulfilled:

$$S^{\rm PM} < S^{\rm V} < S^{\rm ASh}. \tag{2.4}$$

They explain the known discrepancy in the values of S yielded by the two first models from the results of independent nonoptical measurements of S.[2,27,67,82,98] We should note that the difference between the values of $\Delta\gamma$ in (2.2) found in the first two models from the refractive indices of monocrystals of mesogenic compounds compensates the difference in values of S in the mesophase, and the first inequality in (2.4) goes over into an approximate equality. Figure 2 shows a comparison of the data on S for the nematic LC of p-azoxyanisole (PAA) obtained by refractometry within the framework of different models of the local field with the results of independent measurements.

For cholesteric liquid crystals the analog of (1.23) is the relationship[28,101]

$$\Delta\varepsilon_x = 4\pi N\left[\gamma\Delta f - \frac{1}{2}S\Delta\gamma\left(\bar{f} + \frac{\Delta f}{3}\right)\right]_x, \tag{2.5}$$

which is written in the coordinate system of the optic axis of the planar texture. Upon taking account of (1.12) and $\Delta\varepsilon_x = -\Delta\varepsilon_H/2$,[2,102] we find that the relative contribution of the anisotropy Δf_x to $\Delta\varepsilon_x$ coincides with the relative contribution of Δf_n to $\Delta\varepsilon_n$ within the limits of a quasinematic layer. For cholesteric LCs with a small birefringence of the

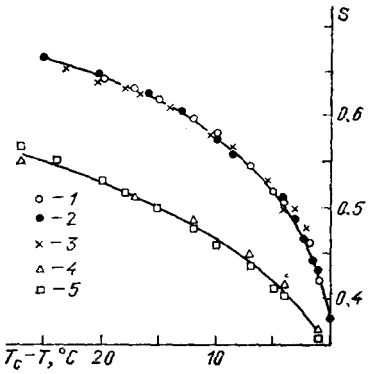

FIG. 2. Temperature dependence of the order parameter of PAA. *1*—calculation by (1.32)–(1.34) and (2.1), *2*—^{13}C NMR data,[98] *3*—NMR of protons of benzene rings,[99] *4*—calculation by (1.22) and (2.1) for $\sigma = 0$,[82] *5*—calculation by (1.39), (1.40), and (2.1);[100] solid lines—interpolation.

type of cholesteryl pelargonate (CP), one can restrict the treatment, according to (1.12) and (1.29), to the isotropic approximation $\Delta f = 0$. As we see from Fig. 3, the values of S for CP found from refractometric data and measured by the nuclear quadrupole resonance method coincide throughout the region of the mesophase. For cholesteric LCs with a large birefringence neglect of the anisotropy $\hat{f}$ within the framework of refractometry leads to depressed values of S_i as compared with the data of NMR.[104]

Above we have treated the effects of the local field involving the sign and the magnitude of Δf. In refractometry also an important role is played by allowing for the dispersion $\Delta f(\lambda)$ (see Sec. 1.2), especially in studying the dispersion dependences $\gamma_{l,t}(\lambda)$ of the components of the molecular polarizability.[40,58] The relation between the true value γ_t, which corresponds to taking correct account of the anisotropy Δf, and the value γ_t^i found in the isotropic approximation has the form

$$\gamma_t^i = \gamma_t + \frac{[\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)]^2}{4\pi N S \bar{f}^2}(\tau_k - \tau). \qquad (2.6)$$

When there is a spectral inversion of the sign of $\Delta f(\lambda)$ at the point $\lambda = \lambda_0$, the inequalities $\tau_k - \tau \lessgtr 0$ and $\gamma_t^H \gtrless \gamma_t$ are fulfilled when $\lambda \gtrless \lambda_0$. If $\Delta f < 0$ for the liquid crystal in the visible region of the spectrum, then with increasing λ the isotropic approximation leads to an elevation of the values of $\gamma_t^i(\lambda)$ as

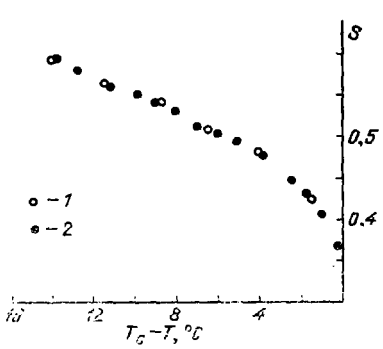

FIG. 3. Temperature dependences of the order parameter S in quasinematic layers of cholesteryl pelargonate from the data of the methods of refractometry[57] (*1*) and nuclear quadrupole resonance[103] (*2*).

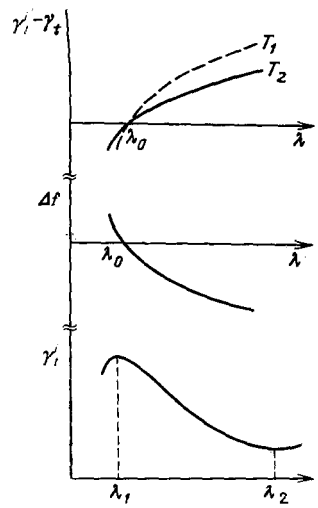

FIG. 4. Qualitative form of the dispersion relationships of the anisotropy Δf, the difference $\gamma_l^i - \gamma_t$, and the component γ_l^i upon spectral inversion of the sign of Δf.

compared with γ_t, and can replace the normal dispersion of $\gamma_l^i(\lambda)$ with an anomalous dispersion at $\lambda = \lambda_2$ (Fig. 4), as has been observed in Refs. 6, 41, 67, and 105. When $\lambda < \lambda_0$, the increment to γ_t in (2.6) is negative and rapidly increases with decreasing λ. This can lead to the appearance of another region of anomalous dispersion of λ_l^i when $\lambda < \lambda_1$ in a region of transparency of the LC as has been observed in Refs. 40 and 43.

The relation between the longitudinal components of γ_l^i and γ_l has the form

$$\gamma_l^i = \gamma_l - \frac{[\bar{\varepsilon} - 1 + (\Delta\varepsilon/3)]^2}{2\pi N S \bar{f}^2}(\tau_k - \tau), \qquad (2.7)$$

and we have $\gamma_l^H \lessgtr \gamma_l$ when $\lambda \gtrless \lambda_0$. Throughout the region of transparency of the LC, the dispersion $\gamma_l^i(\lambda)$ is normal and stronger than the dispersion of the true magnitude $\gamma_l(\lambda)$. Owing to the independence of λ_0 of the temperature of the mesophase (cf. Sec. 1.2), all the graphs of $\gamma_l^i(\lambda)$ corresponding to different temperatures must intersect in the single point $\lambda = \lambda_0$ where the values of $\tau_k(\lambda_0, S)$ coincide with the true values of $\tau(S)$ for the LC being studied. This enables one to determine the components $L_{\parallel,\perp}$ from refractometric data.[43]

2.2. Absorption spectroscopy

Upon taking correct account of the anisotropy of the local field, one can obtain from the polarized infrared and ultraviolet absorption spectra of the LC also quantitative information on the subtle features of the orientational order of the molecules as a whole[26,35,106] and of their individual fragments in different phase states,[107] the orientations of the moments of the vibrational[45,108] and electronic transitions,[109,110] and mutually consistent variations of the structural and molecular parameters.[11,12,89,110–112]

Within the framework of the effective local field, the corrections to the spectral position of the intensity of absorption bands of the LC caused by resonance dipole-dipole interaction of the molecules can be obtained by the method of Ref. 13, which was developed for molecular crystals. The

results of this approach coincide with those obtained within the framework of exciton theory.[35,113-116] Let us study an isolated, nondegenerate transition having the frequency ω_0 in the isolated molecule, where the direction of the transition moment μ is given in the molecular coordinate system by the angle β between μ and the z axis and the angle φ between the x axis and the projection of μ on the xy plane. Renormalization of the molecular spectrum by the static interaction of the molecule with the environment causes the frequency ω_1 of the transition being studied to deviate from ω_0. In the vicinity of the transition being studied, one can represent the components γ_j in (1.8) in the form

$$\gamma_j(\omega) = \gamma_j^{\Phi} + \frac{\omega_p^2 F_j/4\pi N}{\omega_1^2 - \omega^2 + i\Gamma\omega}, \tag{2.8}$$

Here ω_p is the plasma frequency, γ_j^b is the background contribution to γ_j from all the other resonances, A is the oscillator strength of the transition, and we have

$$F_{\parallel} = \frac{A}{3}\left(1 + 2SS_\beta - \frac{2}{3}GG_{\beta\varphi}\right),$$

$$F_{\perp} = \frac{A}{3}\left(1 - SS_\beta + \frac{1}{3}GG_{\beta\varphi}\right), \tag{2.9}$$

$$S_\beta = \frac{1}{2}(3\cos^2\beta - 1), \quad G_{\beta\varphi} = \frac{1}{2}(3\sin^2\beta \cdot \cos 2\varphi). \tag{2.10}$$

Substitution of expressions of the type of (1.7) for $\gamma_j(\omega)$ and γ_j^b into (2.8) yields

$$\varepsilon_j(\omega) = \varepsilon_j^b + \frac{\omega_p^2 F_j (f_j^b)^2}{\omega_j^2 - \omega^2 + i\Gamma\omega}, \tag{2.11}$$

$$\omega_j^2 = \omega_1^2 - \omega_p^2 F_j L_j f_j^b. \tag{2.12}$$

Renormalization of the oscillator strength of the transition is formally reduced to replacing A by the new effective value $A\,(f_j^b)^2$. The position of the maximum ω_{jm} of the absorption line does not coincide with ω_j, while $\omega_j < \omega_{jm}$. For absorption bands that are not too strong[58] we have

$$\omega_{jm} - \omega_j = \frac{f_j^b}{4L_j\varepsilon_j^b}(\omega_1 - \omega_j), \tag{2.13}$$

When $\varepsilon_j^b = 2$, $L_j = 1/3$, the frequency ω_{jm} lies in the middle of the interval $\omega_j \ldots \omega_1$. Since in a liquid crystal usually one has $L_\perp \lesssim 2L_\parallel$, then we have

$$\frac{\omega_{\parallel m} - \omega_\parallel}{\omega_1 - \omega_\parallel} > \frac{\omega_{\perp m} - \omega_\perp}{\omega_1 - \omega_\perp}, \tag{2.14}$$

When the anisotropy of the tensor $\hat{L}$ is large enough, the difference $\omega_1 - \omega_{\parallel m}$ can change sign from positive to negative.

The resonance dipole–dipole interaction of the molecules in the excited state leads to a deviation in the position of the polarized absorption bands[58]

$$\omega_{jm} = \omega_1 - \frac{\omega_p^2 f_j^b L_j F_j}{2\omega_1}\left(1 - \frac{f_j^b}{4L_j\varepsilon_j^b}\right), \tag{2.15}$$

That is, it causes a resonance splitting analogous to the Davydov splitting of exciton absorption bands in molecular crystals.[13] When $0 \leqslant \beta < 54.7°$, the magnitude of the splitting $\Delta\omega = \omega_{\perp m} - \omega_{\parallel m}$ is determined by the balance of the contributions, opposite in sign, of the orientational order of the molecules and of the anisotropy of the local field; here the cases $\Delta\omega \gtrless 0$ are possible. When $\beta = 54.7°$ and $\varphi = 45°$, for which $S_\beta = G_{\beta\varphi} = 0$, the splitting is $\delta\omega < 0$ and it is induced only by the anisotropy of the local field. The case $\beta = 90°$ and $\varphi = 0$, which has not been studied yet, is the most probable situation for observing resonance splitting of absorption bands in liquid crystals.

The integral optical density D_j of a band (or the absorption coefficient) does not depend on the renormalization of the parameters ω_j in the different components of the spectrum. The magnitude of D_j for a real liquid crystal involves the magnitude D_j' for the model corresponding to it of an oriented molecular gas of the same density and with the same effective molecular parameters by the relation[35]

$$D_j = \frac{D_j'(f_j^{\Phi})^2}{n_j^{\Phi}}, \tag{2.16}$$

Here we have $n_j^b = (\varepsilon_j^b)^{1/2}$, with this relationship for $\omega_j \gg \Gamma$ being valid even for intense absorption bands.

For an isolated band of dopant absorption lying in a region of transparency of the liquid-crystal matrix, the position of the maxima of its polarized components is given by the expression[58]

$$\omega_{jm} = \omega_1 - \frac{x\omega_p^2 f_j^b F_j L_j}{2\omega_1}\left(1 - \frac{f_j^b}{4L_j\varepsilon_j^b}\right). \tag{2.17}$$

At a concentration of dopant $x \ll 1$ we have $\omega_{jm} \approx \omega_1$, while the values of ε_j^b practically coincide with the corresponding components $\varepsilon_j(\omega)$ for the matrix in the dopant absorption band. For fixed L_j and F_j the approach of ω_1 from below to the frequency Ω_0 of the intrinsic absorption of the matrix leads to a resonance-type increase in the quantities ε_j^b and f_j^b and an increase in the difference $\omega_1 - \omega_{jm}$, i.e., to an effective repulsion of the dopant absorption band from the absorption band of the matrix. Another interesting consequence of the anisotropy of the local field on the dopant is the difference in the frequencies $\omega_{\parallel m}$ and $\omega_{\perp m}$ for a spherically symmetric dopant molecule having $F_\parallel = F_\perp$. Equation (2.16) is applicable also to dopant absorption.

On the experimental level the corrections of greatest interest are those for the anisotropy of the local field to the dichroism of the absorption bands and the order parameter.[101] Equations (2.16) and (2.8)–(2.10) imply that the integral optical densities $D_\parallel$, $D_\perp$, and D_i of a planarly oriented uniaxial LC can be written in the form[29,117]

$$C\frac{n_\parallel}{\rho f_\parallel^2}D_\parallel = F_\parallel = \frac{A}{3}\left(1 + 2SS_\beta - \frac{2}{3}GG_{\beta\varphi}\right),$$

$$C\frac{n_\perp}{\rho f_\perp^2}D_\perp = F_\perp = \frac{A}{3}\left(1 - SS_\beta + \frac{1}{3}GG_{\beta\varphi}\right), \tag{2.18}$$

$$C\frac{n_i}{\rho_i f_i^2}D_i = F_i = \frac{A_i}{3},$$

Here $C = \text{const}$, and n_i and A_i are the background quantities. In the absence of reasons for a change in the oscillator strength A in the I-N transition,[19,110-112] the experimentally measurable dichroic ratios

$$N_1 = \frac{D_\parallel}{D_\perp}, \quad N_2 = \frac{D_\perp}{D_i}, \quad N_3 = \frac{D_\parallel}{D_i}$$

of the absorption band being studied can be used to calculate

the parameter

$$\Sigma = SS_\beta - \frac{1}{3} GG_{\beta\varphi}, \tag{2.19}$$

The latter has the meaning of the order parameter characterizing the orientational order of the axis parallel to the dipole moment of the transition of the molecule with respect to the director of the liquid crystal. Equation (2.18) implies that

$$\Sigma_1 = \frac{N_1 g_1 - 1}{N_1 g_1 + 2}, \ \Sigma_2 = 1 - N_2 g_2, \ \Sigma_3 = \frac{1}{2}(N_3 g_3 - 1), \tag{2.20}$$

Here the correction factors g_k have the form

$$g_1 = \frac{n_\parallel}{n_\perp}\left(\frac{f_\perp}{f_\parallel}\right)^2,$$
$$g_2 = \frac{\rho_i n_\perp}{\rho n_i}\left(\frac{f_i}{f_\perp}\right)^2, \tag{2.21}$$
$$g_3 = \frac{\rho_i n_\parallel}{\rho n_i}\left(\frac{f_i}{f_\parallel}\right)^2.$$

We must note that the simple formulas of (2.18) (just like (2.16)) are approximate, while the question of their exactness has not yet been solved. At the same time a comparison with independent data for liquid crystals of different chemical classes (see below) allows us to assume that the exactness of Eqs. (2.18)–(2.21) suffices for practical use of them in the spectroscopy of LCs.

We see from Eqs. (2.20) and (2.21) that the anisotropy of the local field substantially affects the parameter Σ_i. Here the corrections for the anisotropy of the LF to the parameter Σ_k substantially depend on the type of dichroic ratio used in the calculation,[89] while for all Σ_k the sign of the corrections to the quantity $\Sigma_{ki}\mathbf{y}_k$ ($\Delta f = 0$) is identical and positive when the true value is $\Delta f < 0$. This situation is typical of liquid crystals in the infrared and visible regions of the spectrum, since the isotropic approximation yields depressed values of Σ_i obtainable from the spectral data, as compared with the independent magnetic and radiospectroscopic data.[2,26,35,44] The models of (1.39) and (1.40) with $\Delta f > 0$ correspond to an even greater discrepancy $\Sigma_k < \Sigma_{ki}$ than the model of (1.22). Here this discrepancy becomes greater with decreasing λ.

If actually $\Delta f \neq 0$, then the isotropic approximation (1.22) leads to a deviation in the values of Σ_i. In particular, when $\Delta f < 0$, Eqs. (2.20) and (2.21) imply that $\Sigma_{1i} < \Sigma_{2i}$, as is confirmed by experiment for pure and doped LCs of different chemical classes.[12,29,89,107,118–120] Such a difference in the parameters Σ_k is nonphysical, while the actual values of $L_{\parallel,\perp}$ must satisfy the system of equations

$$\Sigma_1 = \Sigma_2 = \Sigma_3, \quad \mathrm{Sp}\,\hat{L} = 1, \tag{2.22}$$

of which the three equations $\Sigma_j = \Sigma_k$ are equivalent. This yields a method of determining the effective parameters $\hat{L}$ and $\hat{f}$ in the LC from experimental data of absorption spectroscopy and refractometry.[29,44] For spherically symmetric dopant molecules with $S = G = 0$ we have all $\Sigma_k = 0$, $g_k = 1/N_k$; this method is equivalent to the known spherical-probe method,[2] which was first realized for the dichroism N_1.[26]

2.3. Raman light scattering (rls)

The interest in studying Raman scattering in liquid crystals has been stimulated by the possibility of obtaining information on the mean values $\langle P_{2,4}(\cos\theta)\rangle$ of the Legendre polynomials, where θ is the angle between the long axis of the molecule and the director of the LC. This enables: reconstructing the distribution function for the different molecular fragments;[121–123] obtaining information on the dispersion $\Delta_p = \langle P_2^2\rangle - \langle P_2\rangle^2$ of an oriented distribution of molecules, which determines the static splitting of polarized absorption bands of the LC and other stationarily ordered molecular media;[114,124] and verifying the predictions of theories of the liquid-crystalline state.[47–49,121–123] Such characteristics of LCs of practical importance as the ratio K_3/K_1 of the elastic moduli of nematics,[6,125] which determines the operational parameters of liquid-crystal displays,[2] the temperature variation of the helical pitch of cholesteric LCs, and other properties, strongly depend on the parameters $\langle P_{2,4}\rangle$.

In a uniaxial LC the spontaneous Raman-scattering tensor of the molecule α_{jk} renormalized by the intermolecular interactions with the nearest coordination environment is associated with the corresponding tensor $\alpha s'_{jk}$ in the model of an oriented molecular gas by the relationship[46]

$$\alpha_{jk} = f_{jj}(\omega_s)\,\alpha'_{jk} f_{kk}(\omega), \tag{2.23}$$

Here ω and ω_s are the frequencies of the incident and the scattered light, respectively, polarized along the k and j axes of the coordinate system of the director. Within the framework of the classical theory of Placzek (see Ref. 127), the Raman-scattering tensor of the molecule

$$\alpha'_{jk} = \left(\frac{\partial \gamma_{jk}}{\partial q}\right)_{q=0} q \tag{2.24}$$

is expressed in terms of the derivative of the effective polarizability of the molecule with respect to the normal coordinate of the corresponding normal intramolecular vibration. The Raman-scattering intensities for a molecule in a liquid crystal and in an oriented gas are connected by the relationship

$$J_{ik} = \frac{n_j(\omega_s)}{n_k(\omega)} f_{jj}^2(\omega_s)\, f_{kk}^2(\omega)\, J'_{jk}, \tag{2.25}$$

Here the n_{jk} are the refractive indices of the LC at the corresponding frequencies. When the tensors α'_{jk} and J'_{jk} are symmetric, the anisotropy and dispersion of the tensors $\hat{f}$ and $\hat{\varepsilon}$ break the symmetry of the tensors α_{jk} and J_{jk}. Just as in the case of absorption spectra, the form of the relationship (2.23) is directly connected with the form of the tensor $\hat{f}$ of (1.6), both for liquid and for solid molecular crystals.[128,129] Use of the implicit form of the tensor $\hat{f}$ without concretizing the $\hat{f}(\hat{\varepsilon},\hat{\gamma})$ dependence does not allow one automatically to write a relation (2.23) for it.

The phase difference for different molecules of the molecular vibration under study in spontaneous Raman scattering imparts an incoherent character to it, while the intensity of molecular scattering is $J'_{jk} \sim \langle(\alpha'_{jk})\rangle^2$. The intensity tensor J'_{jk} in a uniaxial LC has four independent components (xx, yx, xz, and zz), which we can represent in free rotation of the molecules around the longitudinal axes in the form[121,122]

$$J'_{jk} = \mathrm{const}\cdot(E_{jk} + F_{jk}\langle P_2(\cos\theta)\rangle + H_{jk}\langle P_4(\cos\theta)\rangle), \tag{2.26}$$

Here the coefficients E_{jk}, F_{jk}, and H_{jk} depend on the geome-

try of the experiment, the orientation of the eigenaxes of the tensor α' with respect to the axes of the molecule, the parameters $a = \alpha'_{xx}/\alpha'_{zz}$ and $b = \alpha'_{yy}/\alpha'_{zz}$ of the tensor α' in the intrinsic coordinate system, and the angle β between the $\bar{z}$ axis of this system and the longitudinal axis of the molecule. The measurable relative quantities are the degrees of depolarization of the Raman lines

$$R_1 = \frac{J_{zx}}{J_{xx}}, \quad R_2 = \frac{J_{xz}}{J_{zz}}, \quad R_3 = \frac{J_{yx}}{J_{xx}}, \tag{2.27}$$

which are connected with the corresponding parameters R'_k by the relationships[46]

$$R'_1 = \left(\frac{f_\perp}{f_\parallel}\right)^2 \left(\frac{n_\parallel + n}{n_\perp + n}\right)^2 R_1 \equiv \Lambda R_1,$$

$$R'_2 = \Lambda^{-1} R_2, \quad R'_3 = R_3, \tag{2.28}$$

Here n is the refractive index of the cell containing the LC and all the quantities n, n_j, and f_j correspond to the frequency of the scattered light. [One can derive Eq. (2.28) from (2.23) and (2.25) by complete analogy to the way in which Eqs. (2.20) and (2.21) were derived for the dichroic ratios.] In the general case there are six unknown parameters ($\langle P_{2,4}\rangle, a, b, \beta, f_\perp/f_\parallel$) and four measurable quantities (R_{1-3} and R_i) dependent on them. Study of Raman scattering by vibrations having a uniaxial tensor α' that does not depend on the phase state and with a known value of β enables one to determine simultaneously the parameters $\langle P_{2,4}\rangle$ and $f_\perp/f_\parallel$.[58]

Neglect of an anisotropy $\Delta f < 0$ leads to strongly lowered values of $\langle P_2\rangle$ and especially of $\langle P_4\rangle$. As an illustration Fig. 5 shows the experimental values of $\langle P_{2,4}\rangle$ for the liquid crystal 4-ethoxy-4'-octyltolan (208T) obtained from Raman data for the stretching vibration of the C≡C bond with the uniaxial tensor α' and $\beta = 0$. Neglect of the anisotropy of f leads to negative values of $\langle P_4\rangle$ near T_c, just as for the liquid crystal 5CB.[130] In the latter case taking account of the anisotropy of f also considerably elevates $\langle P_4\rangle$ and narrows the interval of negative values of $\langle P_4\rangle$ near T_c.[51]

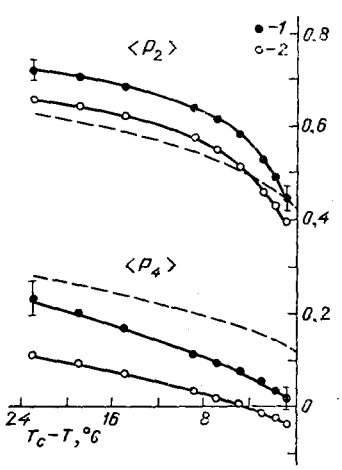

FIG. 5. Temperature dependences of the order parameters $\langle P_{2,4}\rangle$ in the nematic phase of 208T[48] obtained by the Raman-scattering method while taking account (*1*) or not (*2*) of the anisotropy of the local field. The dashed lines correspond to the values of $\langle P_{2,4}\rangle$ in the Maier-Saupe theory.[5]

By using the normalized correlation functions $\langle \alpha'_{jk}(0)\alpha'_{jk}(t)\rangle$ obtained by Fourier analysis of the contours of the polarized components $J_{jk}(\omega)$ of a Raman line,[131,132] one can determine the values of $\langle P_{2,4}\rangle$. In this case the corrections for the local field are eliminated by normalization. For the liquid crystal 208T this method yields values of $\langle P_{2,4}\rangle$[132] that coincide with those shown in Fig. 5, and which take account of the anisotropy of f. Within the framework of the model of (1.32)–(1.34) for a broad set of objects, one can reconcile the values of $\langle P_2\rangle$ measured by methods of absorption spectroscopy and Raman scattering with one another and with the results of nonoptical measurements.[44–47,89,133] The important role of taking account of the anisotropy of the local field in determining the parameters $\langle P_{2,4}\rangle$ is shown within the framework of the methods of polarized luminescence[50] and two-photon absorption.[51] In the former of these the isotropic approximation leads to lowering of both parameters $\langle P_{2,4}\rangle$, and in the latter to strong elevation and a nonphysical temperature dependence of $\langle P_4\rangle$.

3. DETERMINATION OF THE PARAMETERS OF THE LOCAL FIELD IN LIQUID CRYSTALS FROM EXPERIMENTAL DATA

Within the framework of each optical or spectral method of studying LCs, there are such structural or molecular characteristics whose determination from the experimental data in the approximation $\Delta f = 0$ leads to nonphysical consequences if actually the studied object and conditions of performing the experiment (temperature, spectral range, etc.) correspond to $\Delta f \neq 0$. Examples of such characteristics are: the magnitude of the parameter Σ of (2.19) as determined from various dichroic ratios N_k in (2.18), (one-photon absorption[2,29]); the magnitude and temperature dependence of the parameter $\langle P_4\rangle$ (two-photon absorption[51]); the dispersion of the transverse component γ_t of the molecular polarizability (refractometry[40]). All the methods known and realized up to now of experimental determination of the parameters of the local field[2,29,40] that satisfy the requirements of Sec. 1.5 are based on detecting and eliminating the noted nonphysical consequences from experiment. However, the choice of the structural or molecular characteristics needed for analysis within the framework of a previously assigned method is not trivial, as is explained by the currently restricted number of methods of experimental study of the local field in liquid crystals. The expansion of these potentialities directly involves the theoretical study of the influence of the anisotropy of the local field on the broader set of structural and molecular parameters of LCs that can be determined within the framework of molecular optics. Thus all three aspects of the problem of the local field in liquid crystals noted at the end of Sec. 1.5 are closely interrelated.

3.1. The spherical-probe method

This method[2] is based on measuring the dichroism N_k in (2.18) of the absorption of a dopant probe molecule that satisfies a number of requirements: symmetry no lower than tetrahedral with $S = G = 0$; absence of distortions of the shape of the molecule in the anisotropic molecular environment of the matrix; absence of specific intermolecular dopant-matrix interactions of the type of complex formation, appearance of hydrogen and other quasichemical bonds; ex-

istence of intense isolated vibrational or electronic absorption bands of the dopant in a region of transparency of the matrix; good solubility of the dopant in the matrix, and minimal distortions of the structure of the matrix by the dopant molecules. In this case the dichroism of the dopant absorption is fully determined by the anisotropy of the local field at the dopant, and we have $g_k = 1/N_k$ (2.21). This method was first realized[26] with the rigid spherically symmetric ions $(PMo_{12}O_{40})^{3-}$ in nematic mixtures near an intrinsic absorption band of the matrix in a region of large values of Δn and strong dispersion of $n_{\parallel,\perp}(\lambda)$. The obtained value $f_\perp/f_\parallel \approx 1$ corresponds to the expected isotropization of the tensor f in the ultraviolet region of the spectrum (see Sec. 1.2). Subsequently[113] this method was applied to studying the local field at octahedral molecules of $Mo(CO)_6$ in stretched polyethylene films with $\Delta n \approx 0.02$. The obtained value $f_\perp/f_\parallel = 1$ corresponds to the isotropization expected on the basis of (1.29) and (1.30) of the tensors f and L in an anisotropic molecular medium having small Δn.

The second of the requirements on the probe noted above is difficult to control. This introduces an uncertainty into the interpretation of the measured dichroism of the dopant molecules, which are highly symmetric in the gas phase or in an isotropic solvent. The distortion of tetrahedral probes has been studied in detail by the NMR method with the examples of tetramethylsilane $Si(CH_3)_4$ and neopentane $C(CH_3)_4$ in nematic[134] and smetic[135] matrices, and also with a large number of other molecules and ions in thermotropic and lyotropic liquid crystals.[58] In a uniaxial environment of a liquid crystal the symmetry of molecules T, T_d, and T_h is lowered to C_{3v} or D_{2d}. Neglect of the resulting onset of $S > 0$ and dichroism $N_1 > 1$ leads to a factitious positive increment to the true value of Δf and correspondingly to a lowering of the determined anisotropy of the tensor L.[58,136,137] At the same time, for a liquid crystal having a small magnitude of Δn and Δf, one can use the observed dichroism of highly symmetric dopant molecules to study the character of the distortions.[138,139]

The use of dopant molecules of symmetry O, O_h, T, T_d, or T_h is Raman spectroscopy to determine the parameters of the local field is complicated by the fact that, even when they are not distorted in the matrix when $\langle P_2 \rangle = 0$, such molecules have $\langle P_4 \rangle \neq 0$, while small distortions of the dopant and its partial orientation lead to a substantial change in the observed degrees of depolarization R_k of the Raman bands of the dopant.[58]

3.2. The spectral method

To determine the effective parameters L and $\hat{f}$ when using Eqs. (2.18)–(2.22), only the macroscopic parameters of the liquid crystal are needed. This gives rise to the following advantages of this method: mutually coordinated determination of the true parameters $\hat{L}$ and $\hat{f}$ and of the values of Σ corresponding to them; independence of the method of the form and chemical structure of the molecules and of the form of the normal vibration; the possibility of determining the parameters of the local field for the intrinsic and the dopant molecules, and for various molecular fragments; and the use of electronic or vibrational transitions in different spectral regions to study the dispersion $\hat{f}(\lambda)$. The sole restriction is the independence of the oscillator strength of the transition being studied of the phase state of the liquid crystal. In the vibrational spectrum of molecules, absorption bands always exist that satisfy this condition, and the use of infrared spectroscopy is preferable in the experimental study of the features of the local field in a liquid crystal. Moreover, when $\Delta f < 0$ the corrections to Σ are maximal in the infrared region, which increases the accuracy of determining the parameters $\hat{L}$ and $\hat{f}$.

Convenient objects for verifying the correctness of the method under study are the liquid crystals 4-n-alkyl and 4-n-alkoxy-4′-cyanobiphenyls (n-CB and n-OCB) (8OCB), which have been studied in detail by nonoptical methods[140] and by the Raman-scattering method in the stretching vibration of the C≡N bond in the isotropic-local-field approximation. The isolated infrared absorption band ($\lambda_{max} = 4.5$ μm) corresponding to this vibration satisfies the spectral requirements for realizing the discussed method of determining L, with $\beta = 0$ and $\Sigma = S$. Figures 6 and 7 show the temperature dependences of S and $L_\perp$ for the objects being studied, as found by (2.18)–(2.22). For 7CB the value of $S_1 = S_2$ fully agrees with the results of the magnetic measurements[140] throughout the region of the nematic phase. The values of S_i obtained by the Raman-scattering method[141] are substantially lower than those found from the infrared dichroism. For the studied type of vibrations one can take account of the correction for the anisotropy of the local field to the Raman scattering by the formula[89]

$$S = S_i - 2\frac{3(1-S_i)R'_{1i} + 4(1+2S_i)R'_{2i}}{3R'_{1i} + 12R'_{1i}R'_{2i} + 8R'_{2i}}\frac{\Delta f}{\bar{f}}, \quad (3.1)$$

Here R_{ki} is the degree of depolarization in (2.28) when $f_\perp = f_\parallel$. The use of the parameters S_i and R'_{ki} given in Ref. 141 and the experimental values of $L_\perp$ shown in Fig. 6 in calculating S by (3.1) leads to agreement of the results of the three independent methods, of which the two spectral methods pertain to different (visible and infrared) regions of the

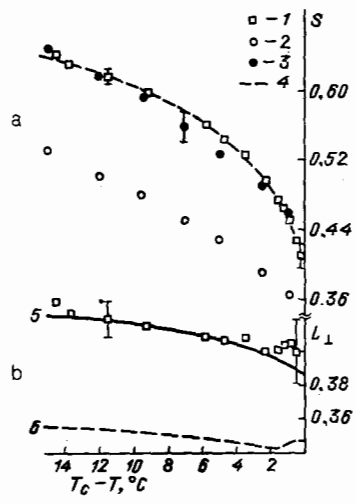

FIG. 6. a—Temperature dependences of the order parameter S in the nematic phase of 7CB obtained by different methods: *1*—from infrared dichroism by (2.22) with account taken of the anisotropy of the local field; from Raman scattering without taking account[141] (*2*); and with account taken (*3*) of the anisotropy of the local field by (3.1); *4*—interpolation of the results of magnetic measurements.[140] b—Temperature dependences of the experimental values and the theoretical values calculated by (1.32) and (1.36) (*5*) and those by (1.37) (*6*) of $L_\perp$.

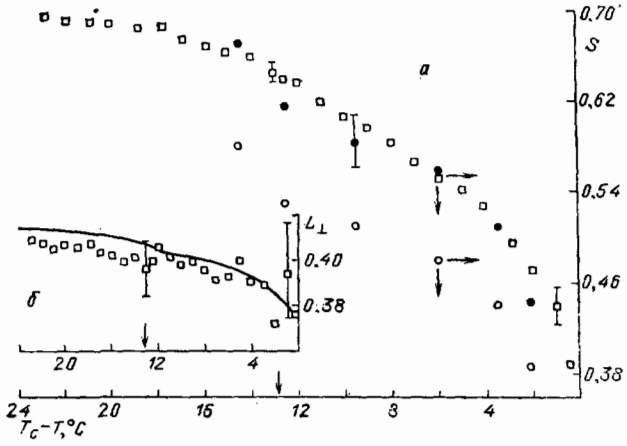

FIG. 7. Temperature dependences of the order parameter S (a) and of the component $L_\perp$ (b) of the Lorentz tensor in the mesophase of 8OCB. The symbols are the same as in Fig. 6. The arrows indicate the N-S_A transition temperature.

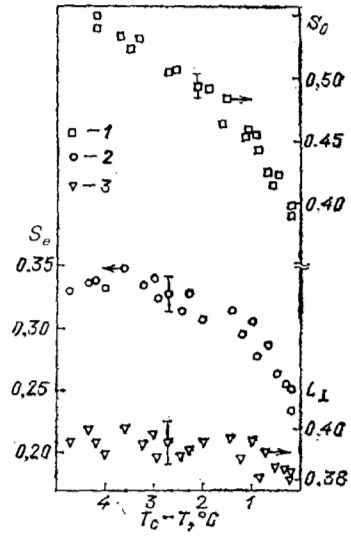

FIG. 8. Temperature dependences of the orientational order parameters of the rigid molecular skeletons S_0 (*1*) and of the end fragments of the flexible chains of the molecules S_e (*2*), as well as of the component $L_\perp$ (*3*) of the Lorentz tensor in the nematic phase of the mixture LC-1.

spectrum. For 8OCB the deviation of the quantities $S_1 = S_2$ from the parameter S_i measured by the Raman-scattering method[141] is also eliminated when one takes account of the correction for the local field according to (3.1).

The parameters $L_\perp$ calculated by Eqs. (1.3), (1.33), and (1.34) agree with those found by experiment. The models of (1.39) and (1.38) correspond to lowered values of $L_\perp$ and a nonmonotonic behavior of $L_\perp(\Delta T)$. The nematic-smectic A (N-S_A) phase transition in 8OCB has practically no effect on the variation of the parameter $L_\perp$, which depends mainly on the orientational order of the molecules.

Study of the cyanophenyl ester of heptylcinnamic acid[12] (CPEHCA) having a broad interval of the nematic phase and variation of S confirmed the relationship (1.28) throughout the nematic phase, apart from a narrow temperature interval near T_c.

In the cyanophenyl ester of hexyloxybenzoic acid[142] (CPEHOBA), which is isomorphous with the molecules of the mixture[26] studied by the spherical-probe method, the values of $L_\perp$ for the intrinsic molecules of the LC coincided with the same for the dopant molecule of the probe. This contradicts the statement[6] that the anisotropy of the local field at the dopant in a nematic phase involves the anisotropy of the shape of the dopant molecule, and it supports the conclusion[13] that the local field at the dopant is determined mainly by the properties of the matrix.

Study of the local field at the C≡N end fragments of flexible chains of molecules in a nematic mixture of two homologs (LC-1) showed[107] that, despite the weak orientational order of these fragments as compared with the order of the molecular skeletons (Fig. 8), the found values of $L_\perp$ agree well in magnitude and in the dependence $L_\perp(\Delta\varepsilon)$ at fixed S_0 with the data of analogous measurements on LC-1 with the marker C≡N in the molecular skeleton. This implies that the same effective local field acts on the different fragments of molecules in nematic liquid crystals.

In studying the isomorphous nematic mesogens[29,44,117] (5BCO), which differ substantially in the electronic structure of the molecular skeleton, the anisotropy of the polarizability $\Delta\gamma$, and the magnitude of Δn, an isotropization of the tensors $\hat{L}$ and $\hat{f}$ was found in going from 5CB to 5BCO, which is accompanied by a decrease in $\Delta\gamma$ and Δn. Here the values of S for these liquid crystals differ insignificantly. An effect of isotropization of $\hat{L}$ and $\hat{f}$ was found also in probing a nematic mixture of trans-alkylcyclohexanecarboxylic acids (CHCAs) having a small value of Δn with disk-shaped dopant molecules of derivatives of azulene.[11] This also confirms the conclusion of the determining role of the matrix in the formation of the local field at the dopant and the independence of the local field of the shape and character of the orientational order of the dopant molecules.

At fixed S and λ the dependence of the tensors $\hat{L}$ and $\hat{f}$ on the electronic structure of the molecules must be manifested in their dependence on the magnitude of $\Delta\varepsilon$. Such a dependence for pure and doped liquid crystals is shown in Fig. 9. Within the limits of experimental error it has a linear character, which agrees with (1.30). For values $m = 3$–6 typical of mesogenic molecules, the model of (1.33) and (1.35) with $S = 0.5$ functions in the interval $\Delta\varepsilon = 0.45$–0.8, which explains its successful use for LCs with large birefringence.[42–47,123,133] We see in Fig. 9 a need to take account of the electronic structure of the molecules in the theory of the local field in anisotropic molecular media.

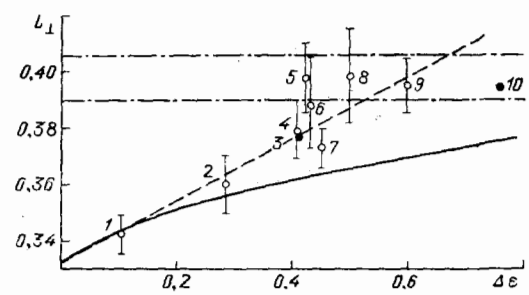

FIG. 9. Correlation of the experimental components $L_\perp$ (open symbols) and those calculated by (1.32) and (1.36) (solid symbols) of the Lorentz tensor with the corresponding values $\Delta\varepsilon = n_\parallel^2 - n_\perp^2$ for $S = 0.5$ and $\lambda = 589$ nm for different LCs: *1*—mixture CHCA,[11] *2*—5BFO,[29,117] *3*—NFOOB,[129] *4*—CPEHOBA,[142] *5*—7CB, *6*—8OCB,[44] *7*—CPEHCA,[12] *8*—5CB,[44] *9*—mixture LC – 1[107] *10*—PAA.[27] Solid line—interpolation of values of $L_\perp$ corresponding to the approximation $\Delta f = 0$; the dot-dash lines enclose the interval of values of $L_\perp$ calculated by (1.32) and (1.36) for $m = 3$–6.

3.3. The refractometric method

The spectral method is governed by the effective parameters $\hat{L}$ and $\hat{f}$ for the fragment of the molecule associated with the band of the electronic or vibrational transition under study. The refractometric method (Sec. 2.1)[40,43] yields the same parameters averaged over the molecular volume. A comparison of (1.26) and (1.27) with (2.6) shows that the increment to γ_i depends weakly on the temperature. Therefore, owing to the weak dispersion of γ_i, to a possible dependence of γ_i on the phase state, or to insufficient accuracy of measuring the parameters S and $\varepsilon_{\parallel,\perp}$, one may not observe an intersection of the graphs of $\gamma_i^j(\lambda, T_j)$ at a single point (see Fig. 4). In this case the appearance of a maximum of λ_1 and of a region of anomalous dispersion of γ_i^j for $\lambda < \lambda_1$ indicates the closeness of λ_1 to λ_0; for an estimate one can take $\tau(\Delta T) = \tau_k(\lambda_1, \Delta T)$.

Figure 10 shows the $\gamma_i^j(\lambda)$ dependence for 5CB and the presented objects[43] 8CB, C-4, and MBBA having quite similar anisotropies of molecular shape, yet differing in the electronic structure of the aromatic skeleton. For all the $\gamma_i^j(\lambda)$ dependences one observes maximum points of λ_1 and anomalous-dispersion regions for $\lambda < \lambda_1$, which indicates the dispersion of the quantity Δf and a spectral sign inversion. The estimate $\tau = \tau_k(\lambda_1)$ yields a magnitude of $L_\perp$ for 5CB that agrees with that found by the spectral method.[44] For 8CB the position of λ_1 does not change upon the N-S_A transition, which correlates with the data of the spectral method for 8OCB. For MBBA the value $f_\perp/f_\parallel = 1.03$ for $\Delta T = 17°$ and $\lambda = 589$ nm agrees with calculation by Eq. (1.29).[40] The smallness of the anisotropy Δf for MBBA lends clarity to the discussion[53] of the need to take account of the anisotropy of the local field in a given liquid crystal in determining the parameters $\langle P_{2,4} \rangle$ by the method of generating a third optical harmonic. For C-4, which has a small birefringence throughout the interval of the nematic phase, we have $L_\perp \approx 1/3$ and $\Delta f \approx 0$, which corresponds to isotropization of the tensors L and f in going from CPEHOBA to C-4 with decreasing $\Delta\gamma$. All the general properties of the tensors $\hat{L}$ and $\hat{f}$ established by the refractometric method agree with those found by the independent spectral methods.

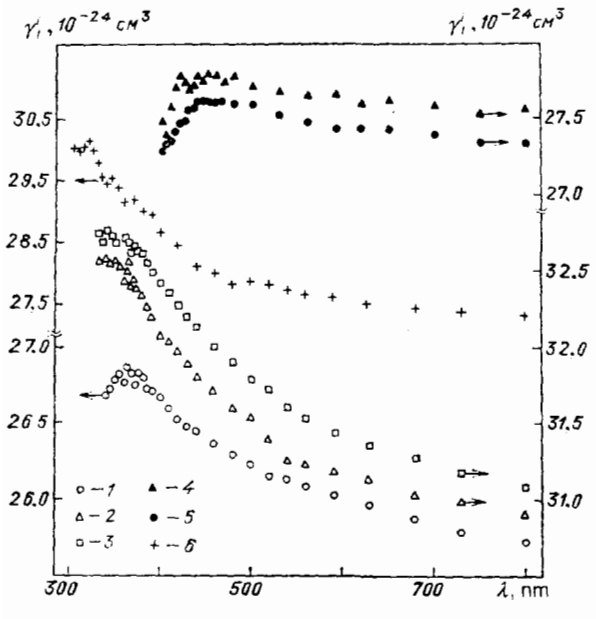

FIG. 10. Dispersion relationships of the transverse components $\gamma_i^j(\lambda)$ of the effective polarizability of the molecules in the mesophase of 5CB (*1*, $T_c - T = 8°$), 8CB (*2*, 4°; *3*, 11°), and MBBA (*4*, 2°; *5*, 17°), and C-4 (*6*, 2°).

CONCLUSION

In this review we have tried to demonstrate the importance of taking account of the effects of the local field in the qualitative and quantitative interpretation of the optical and spectral properties of liquid crystals. The need to take account of these effects becomes evident also in analyzing multiquantum and nonlinear processes in LCs, for which the magnitude of the corrections for the local field rapidly increases and their dispersion and anisotropy become more important.[51,145,146] Of course, taking a global account of the effects of the local field in all these cases is possible only under the condition of detailed theoretical description. In this regard we apparently stand at the onset of a transition stage. On the one hand, the appearance of a relatively consistent theory of the high-frequency permittivity of liquid crystals presented in Sec. 2 amounts to substantial progress as compared with the set of mutually contradictory semiphenomenological models that had previously been discussed in the literature. The statistical theory made it possible to understand more deeply and to systematize the fundamental qualitative properties of the local field in liquid crystals, to establish analogies with the molecular optics of crystals, to determine the role of different intermolecular correlations, and to develop a procedure for obtaining approximate expressions for the refractive indices, the Lorentz tensor, and other quantities, both for one-component LCs and for mixtures of them. The general theory could also be used to reveal the approximations that certain of the semiphenomenological approaches are actually based on. At the same time, the essential theory remains highly schematic, since it pertains to a system of idealized molecules whose polarizability is invariant and concentrated at the center of mass. We note that analogous simplifications are characteristic also of the existing theory of the permittivity of isotropic liquids. At present, however, sufficient experimental data have been amassed that indicate the need for taking account of the distribution of polarizability through the molecular volume,[143,144] and also, perhaps, of the contribution of the higher multipoles and the influence of random fields created by adjacent molecules on the dispersion of the molecular polarizability. The latter can be especially important in studying phenomena near molecular resonances. A hindering factor in the development of the theory is also the lack of enough information on the character of the short-range correlations in LCs that substantially affect the parameters of the local field. The noted limitations of the theory do not allow a complete quantitative description of the local field in liquid crystals. At present many important problems can be solved only by comparison with experiment, as was noted in Sec. 3. Here an important linking element are the concepts of the effective local field and the effective Lorentz tensor in the liquid crystal, which have been used implicitly in a number of experimental studies, and which have been formulated rigorously within the framework of the statistical theory.

In the field of experimental studies of the effects of the local field in liquid crystals in recent years, a qualitative jump has also occurred involving rather effective and rela-

tively simple methods of experimental determination of the parameters of the effective local field. The use of these methods within the framework of ultraviolet and infrared absorption spectroscopy, Raman spectroscopy, refractometry, etc., for a large number of liquid crystals of different structures has enabled obtaining the values of the effective molecular parameters and the order parameters, which agree among themselves and with the results of independent measurements. At the same time, the boundaries of applicability of these new methods described in Sec. 2 remain unclear, since they are based on a set of approximate expressions whose accuracy is hard to establish at this stage of development of the theory. At present these methods have already been used to obtain a large amount of experimental data for different phases of LCs, and, with small changes, analogous methods already today can be used in studying the local field in mono- and multimolecular films of surface-active substances and the specially prepared structures of Langmuir-Blodgett films.[147-149] These objects, along with liquid crystals, are examples of partially ordered molecular media that are promising for use as the elementary basis of molecular electronics. At the same time, the development of studies, not broadly but deeply, will demand a considerably more developed theory, in which the various effects mentioned above are taken into account, albeit partially.

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