

Theory of the dielectric susceptibility of nonpolar biaxial liquid crystals

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A statistical theory of the dielectric susceptibility of nonpolar liquid crystals, whose constituent molecules are biaxial, is proposed. The ordering is described by means of the mean field theory, in which a set of basic functions is introduced. The dielectric susceptibilities are derived using a generalized Clausius-Mossotti approach. The theory was used to calculate the temperature and the density dependence of the order parameters and of the susceptibilities. On increasing the density, an ordering reversal of the corresponding susceptibilities is obtained.

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I. INTRODUCTION

In liquid-crystal nematic phases the molecule gravity centers do not have long-range order, but there is a partial directional order of the molecules [1]. They tend to be parallel to selected axes, labeled by unit vectors \vec{L} , \vec{M} , and \vec{N} . In the uniaxial nematic phase there is one axis $\vec{N} \equiv -\vec{N}$ (the symmetry of the phase is $D_{\infty h}$), whereas in the biaxial nematic phase all three axes are involved (the symmetry of the phase is then D_{2h}).

A static electric field imposed on a nematic is connected with at least two different processes: namely, the dielectric constant anisotropy and the flexoelectric effect (polarization induced by a distortion). Because of the symmetry, the dielectric permittivity differs in value along the different axes and, generally, it acquires three different values ϵ_λ , $\lambda = x, y, z$. The dielectric anisotropies are defined as

$$\Delta\epsilon_U = \epsilon_z - \frac{1}{2}(\epsilon_x + \epsilon_y), \quad (1)$$

$$\Delta\epsilon_B = \epsilon_y - \epsilon_x. \quad (2)$$

In the uniaxial nematic phase $\Delta\epsilon_B=0$ and the value of $\Delta\epsilon_U$ can be positive [2] or negative [3] for nonpolar or polar substances, respectively. Compounds with a large anisotropy possess a strongly polar group in specific positions [4]. As far as the flexoelectric effect is concerned, it was originally explained as a steric effect due to the asymmetry of the molecular shape [5]. But Prost and Marcerou [6] showed that the polarization of a deformed liquid crystal is also produced as a result of a gradient in the average density of quadrupole moments of molecules. In this paper we deal with nonpolar molecules, while the flexoelectric effect is not considered.

The purpose of the dielectric theory is to relate the macroscopic permittivities (ϵ) or the susceptibilities ($\chi = \epsilon - 1$) to the molecular properties, i.e., to the polarizability α and the dipole moment. When the existing dielectric theory of isotropic liquids is applied to liquid crystals, the degree of ordering must first be taken into account. Next, the question of the internal field experienced by a molecule has to be taken into account. For isotropic liquids, due to the contributions of surrounding molecules, the internal field is not equal to the

macroscopic field [4]. In the case of liquid crystals, this situation is more complicated because of the various anisotropies and the incomplete orientational order.

We would like to propose a dielectric theory for the phases that consist of rigid nonpolar biaxial molecules. Despite the dearth of experimental realizations of biaxial liquid-crystalline phases, they have been extensively studied theoretically. The ordering of these phases has been studied by means of mean field theory [7–9], counting methods [10,11], the Landau–de Gennes theory [12,13], bifurcation analysis [14], and density functional theory [15].

All the theories mentioned above predict that the system exhibits four phases as the molecular biaxiality varies: positive and negative uniaxial phases, respectively, formed by prolate and oblate molecules, as well as biaxial and isotropic phases. The nematic–isotropic (NI) phase transition is expected to be of the first order and weakens as the biaxiality increases until it becomes continuous at the point of maximum molecular biaxiality, the Landau bicritical point. At this point, the system should go directly from the biaxial to the isotropic phase. The biaxial nematic–uniaxial nematic transition is expected to be of second order.

In the Onsager theory, the isotropic–nematic transition is attributed to the tendency of pairs of molecules to minimize their excluded volume (or the second virial coefficient B_2). That is why it is important to know the dependence of B_2 on the orientations of molecules. Tjipto-Margo and Evans [16] calculated the mutual orientation dependence of the second virial coefficient B_2 for hard biaxial ellipsoids. The distribution functions were determined there for the Onsager and the Lee models. They noticed that introduction of the biaxiality has a pronounced effect: both the P_2 order parameter and the first-order nature of the IN transition were greatly reduced from that of comparable uniaxial bodies. In 1997 Vega [17] calculated numerically the first five virial coefficients of the hard ellipsoids. At the same time Zakhlevnykh and Sosnin [18] suggested a method that enables one to calculate exactly the second virial coefficient for the system of biaxial ellipsoidal particles, as well as to obtain a simple approximation formula for the third one.

Taylor and Herzfeld [19] studied the liquid-crystalline phase behavior of biaxial hard particles (spheroplatelets) using a scaled particle calculation of the configurational entropy, combined with the cell description of translational or-

der. If the translational ordering was ignored, the density vs particle biaxiality phase diagram showed a cusp-shaped biaxial nematic phase intervening between the two uniaxial nematic phases. When the possibility of translational order was considered, the phase diagram showed three distinct smectic-A (Sm-A) phases, in addition to the two uniaxial phases, and only a small remnant of the biaxial nematic phase.

The elastic constants of a liquid crystal determine the change in the Helmholtz free energy of a nematic phase as the liquid crystal is exposed to deformations of its orientational field. The understanding of the elastic constants of liquid crystals is important for a number of reasons. In the first place, they appear in the description of virtually all phenomena where the variation of the director is manipulated by external fields (cf. display devices). Second, they provide unusually sensitive probes of the microscopic structure of the ordered state. Valuable information regarding the nature and importance of various anisotropies of the intermolecular potentials and of the spatial and the angular correlation functions can be derived from a study of the elastic constants. Knowledge of the liquid-crystal elasticity is also needed in the study of defects in them [20]. The theory of the elastic constants for biaxial nematic phases was developed in a number of papers [21–27]. The microscopic expressions for the elastic constants were given and their splitting was predicted at the uniaxial-biaxial nematic transition for some model systems [26].

The hydrodynamics of biaxial nematics was obtained in [28,29]. Viscous properties of nematic liquid crystals composed of biaxial molecules were studied by Fiałkowski [30] and the formulas for the Leslie viscosity coefficients were provided there.

The possibility of a biaxial nematic mesophase has been confirmed by Monte Carlo simulations of a lattice system composed of biaxial molecules [31–33] and of a fluid system of biaxial spherocylinders [34].

Our aim is to present the theory of the static susceptibility of nonpolar biaxial nematic liquid crystals. A discussion of the results for uniaxial nematic liquid crystals and for solid crystals can be found in [4]. The most important results were given by Maier and Meier [3] who extended the Onsager theory of susceptibility to polar nematic liquid crystals. We can write their results in the following form, which can be used for isotropic, uniaxial, and biaxial nematic phases:

$$\epsilon_0\chi_\lambda = \frac{N}{V}hF(\epsilon_0\langle\alpha_\lambda\rangle + \beta F\langle\mu_\lambda\mu_\lambda\rangle), \quad (3)$$

where μ is the permanent dipole moment of a molecule, and h and F are the factors introduced by Onsager and can be written as

$$h = \frac{3\tilde{\chi} + 3}{2\tilde{\chi} + 3}, \quad (4)$$

$$F = \frac{1}{1 - \tilde{\alpha}\epsilon_0f}, \quad (5)$$

$$\epsilon_0f = \frac{2\tilde{\chi}}{2\tilde{\chi} + 3} \left(\frac{3N}{V} \right). \quad (6)$$

In the expressions for h , F , and f the averaged susceptibility $\tilde{\chi}$ and the polarizability $\tilde{\alpha}$ were used, i.e., the anisotropy was neglected. Apart from that, the molecule under consideration was contained in a *spheroidal* cavity. This is unrealistic for liquid crystals and that is why we would like to present a different approach. We note that Maier and Meier (following Onsager) took into account the polarization of the surroundings by the permanent and induced dipole moments. This leads to the presence of a reaction field. In the case of nonpolar molecules the reaction field is small and it is neglected in our calculations.

Dealing with biaxial or less symmetric systems, one has to use the standard rotation matrix elements $D_{\mu\nu}^{(j)}$ [35] which depend on the three Euler angles. Some authors, in order to deal with the real functions with the desired symmetry, define different linear combinations of these functions [14,33]. We would like to introduce real basic functions $E_{\mu\nu}^{(j)}$, which are equivalent to $D_{\mu\nu}^{(j)}$, but have comfortable properties (see Appendix A).

The organization of this paper is as follows. In Sec. II the mean field theory of nematic ordering is provided. In Sec. III the relation among the susceptibility, the polarizability, and the order parameters is established. Section IV is devoted to selected applications of the presented theory. Section V contains a summary. The Appendixes provide the definitions and the main properties of the basic functions (see Appendix A), the shape factors for the susceptibilities (see Appendix B), and the model for the molecular polarizabilities (see Appendix C).

II. THE MEAN FIELD THEORY

The ordering of nematic liquid crystals can be described by means of at least two types of theories [1]. In the Onsager approach the only forces of importance correspond to the steric repulsion and the molecules are similar to very long rods. In the molecular-statistical theory of Maier and Saupe the nematic-isotropic transition is attributed to the anisotropic part of the dispersion forces, the London–van der Waals forces. We use an approach similar to that of Maier and Saupe.

Let us consider a system of N molecules contained in a volume V at temperature T . We assume that the potential energy of the interactions $V(R_1, R_2)$ depends only on the molecule orientations R_1, R_2 . What is more, this energy does not depend on the reference frame orientation

$$V(RR_1, RR_2) = V(R_1, R_2).$$

This leads to the general form

$$V(R_1, R_2) = \sum_j \sum_{\mu\nu} v_{\mu\nu}^{(j)} E_{\mu\nu}^{(j)}(R_2^{-1}R_1), \quad (7)$$

where $E_{\mu\nu}^{(j)}$ are the real functions described in Appendix A. For unitary phases there is the following property:

$$v_{\nu\mu}^{(j)} = v_{\mu\nu}^{(j)} \operatorname{sgn}(\mu)\operatorname{sgn}(\nu). \quad (8)$$

The one-particle distribution function f is defined in such a way that $f(R)dR$ gives the probability of finding the molecule orientation within the range $[R, R+dR]$. It has the normalization

$$\int dR f(R) = 1. \quad (9)$$

We calculate the mean of a selected function $A=A(R)$ as

$$\langle A \rangle \equiv \int dR f(R)A(R). \quad (10)$$

The system state is described by the order parameters $\langle E_{\mu\nu}^{(j)} \rangle$. The free energy of the system consists of the internal energy term and the entropy term

$$F = \frac{N}{2} \int dR_1 dR_2 f(R_1)f(R_2)V(R_1, R_2) + Nk_B T \int dR f(R) \ln[f(R)C_N], \quad (11)$$

where the constant C_N is inserted to give the correct units. The mean field acting on the molecule has the form

$$W(R) = \sum_j \sum_{\mu\nu} w_{\mu\nu}^{(j)} E_{\mu\nu}^{(j)}(R). \quad (12)$$

We derive from the Boltzmann distribution that

$$f(R) = \exp[-\beta W(R)]/Z, \quad (13)$$

where $\beta=1/k_B T$ and the normalization factor is

$$Z = \int dR \exp[-\beta W(R)]. \quad (14)$$

The consistency condition has the form

$$W(R_1) = \int dR_2 f(R_2)V(R_1, R_2). \quad (15)$$

We get the set of equations for the mean field coefficients

$$w_{\mu\nu}^{(j)} = \sum_{\rho} \langle E_{\mu\rho}^{(j)} \rangle v_{\rho\nu}^{(j)} \frac{1}{2} [-\operatorname{sgn}(\mu)\operatorname{sgn}(\nu) + \operatorname{sgn}(\rho)\operatorname{sgn}(\nu) + \operatorname{sgn}(\mu)\operatorname{sgn}(\rho) + 1]. \quad (16)$$

In order to solve our model we should find an orientationally stable solution with minimal free energy.

Now we would like to discuss how to use the molecule symmetry to limit the number of mean field coefficients. Let R_{mol} denote the rotation from the molecule symmetry group

$$V(R_1 R_{mol}, R_2) = V(R_1, R_2 R_{mol}) = V(R_1, R_2). \quad (17)$$

Thus

$$E_{\mu\nu}^{(j)}(R R_{mol}) = E_{\mu\nu}^{(j)}(R_{mol}^{-1} R) = E_{\mu\nu}^{(j)}(R). \quad (18)$$

For biaxial molecules we use $R_{mol}=R_z(\pi)$ and $R_{mol}=R_x(\pi)$, and we recover the Straley model of biaxial nematics [8].

The nonzero coefficients from the potential energy are $v_{00}^{(0)}$, $v_{00}^{(2)}$, $v_{02}^{(2)}=v_{20}^{(2)}$, and $v_{22}^{(2)}$. Note that the rotations imply the D_2 symmetry group but, in fact, we end up with the D_{2h} symmetry group [26].

III. THE DIELECTRIC SUSCEPTIBILITY

The static electric polarization induced by the external field \vec{E} in an isotropic liquid is given by

$$\vec{P} = \chi \epsilon_0 \vec{E}. \quad (19)$$

\vec{P} and χ can be divided into the part due to the molecular polarizability (the induced part) and the part due to the dipole moment (the orientation part). In this paper we deal with the induced part of the polarization and of the susceptibility.

In an anisotropic medium the dielectric susceptibility (permittivity) is a second-rank tensor. We use the laboratory reference frame $(\vec{e}_x, \vec{e}_y, \vec{e}_z)$ and we set the direction of the nematic phase by means of the relations $\vec{L}=\vec{e}_x$, $\vec{M}=\vec{e}_y$, and $\vec{N}=\vec{e}_z$. The equation for the polarization has the form

$$P_\lambda = \chi_\lambda \epsilon_0 E_\lambda, \quad \lambda = x, y, z. \quad (20)$$

On the other hand we can write

$$P_\lambda = \frac{N}{V} \langle p_\lambda \rangle, \quad \lambda = x, y, z, \quad (21)$$

where p_λ are the components of the electric moment induced in the selected molecule. The moment \vec{p} depends on the molecular polarizability tensor α and the internal field \vec{E}^{int} . Our aim is to find the relation between \vec{E}^{int} and \vec{E} in order to connect χ with α . We generalize the Clausius-Mossotti approach by the assumption that the molecule is in a nonspherical cavity of molecular dimensions and surrounded by the anisotropic polarized continuum.

Let us describe the molecule orientations by the set of three unit orthogonal vectors $(\vec{l}, \vec{m}, \vec{n})$,

$$\begin{aligned} \vec{l} &= \sum_{\lambda} R_{1\lambda} \vec{e}_\lambda = \sum_{\lambda} l_\lambda \vec{e}_\lambda, \\ \vec{m} &= \sum_{\lambda} R_{2\lambda} \vec{e}_\lambda = \sum_{\lambda} m_\lambda \vec{e}_\lambda, \\ \vec{n} &= \sum_{\lambda} R_{3\lambda} \vec{e}_\lambda = \sum_{\lambda} n_\lambda \vec{e}_\lambda, \end{aligned} \quad (22)$$

where the matrix elements $R_{i\lambda}$ ($i=1, 2, 3$ and $\lambda=x, y, z$) satisfy the conditions

$$\sum_{\lambda} R_{i\lambda} R_{j\lambda} = \delta_{ij}, \quad (23)$$

$$\sum_i R_{i\lambda} R_{i\beta} = \delta_{\lambda\beta}. \quad (24)$$

The above relations express the orthogonality and the completeness of the local frame.

If the macroscopic field \vec{E} and the polarization \vec{P} are oriented along the z axis, the i th component of the internal field \vec{E}^{int} can be expressed as

$$E_i^{int} = E_i + P_i \Omega_i / \epsilon_0, \quad = (E + P \Omega_i / \epsilon_0) R_{iz}, \quad i = 1, 2, 3, \quad (25)$$

where Ω_i are the shape factors which depend on the cavity shape. Exemplary formulas for the ellipsoid and the rectangular box are given in Appendix B.

The electric field \vec{E}^{int} induces the electric moment \vec{p} with the components

$$p_i = \alpha_i \epsilon_0 E_i^{int}, \quad i = 1, 2, 3, \quad (26)$$

Then, the component along the z axis is of the form

$$p_z = \sum_i p_i R_{iz} = \sum_i \alpha_i (\epsilon_0 E + P \Omega_i) R_{iz}^2. \quad (27)$$

From Eqs. (20), (21), and (27) we obtain

$$\chi_z = \frac{N}{V} \sum_i \alpha_i (1 + \chi_z \Omega_i) \langle R_{iz}^2 \rangle. \quad (28)$$

In a similar way we find χ_x and χ_y , and we get the general formula

$$\chi_\lambda = \frac{(N/V) \sum_i \alpha_i \langle R_{i\lambda}^2 \rangle}{1 - (N/V) \sum_i \alpha_i \Omega_i \langle R_{i\lambda}^2 \rangle}, \quad \lambda = x, y, z. \quad (29)$$

All elements $R_{i\lambda}^2$ can be expressed by means of the selected four R_{1x}^2 , R_{1z}^2 , R_{3x}^2 , and R_{3z}^2 , or by means of the functions $E_{00}^{(2)}$, $E_{02}^{(2)}$, $E_{20}^{(2)}$, and $E_{22}^{(2)}$ (see [26] and Appendix A).

For the completely ordered phase $\langle R_{i\lambda}^2 \rangle = \delta_{i\lambda}$ and we get

$$\alpha_\lambda = \frac{V \chi_\lambda}{N + \Omega_\lambda \chi_\lambda}, \quad \lambda = x, y, z. \quad (30)$$

It is possible to determine α from Eq. (30) by taking χ from the solid state [4].

In the small density limit, the susceptibility is small and then from Eq. (29) we obtain the simplified result

$$\chi_\lambda = \frac{N}{V} \sum_i \alpha_i \langle R_{i\lambda}^2 \rangle \equiv \frac{N}{V} \langle \alpha_\lambda \rangle, \quad \lambda = x, y, z. \quad (31)$$

Let us define the anisotropies

$$\Delta \alpha_U = \alpha_3 - \frac{1}{2}(\alpha_1 + \alpha_2), \quad (32)$$

$$\Delta \alpha_B = \alpha_2 - \alpha_1. \quad (33)$$

Now we can write the expressions that can be used to estimate the order parameters $\langle E_{00}^{(2)} \rangle$ and $\langle E_{22}^{(2)} \rangle$ from the experimental values of the susceptibilities

$$\begin{aligned} \Delta \chi_U &= (N/V) [\Delta \alpha_U \langle E_{00}^{(2)} \rangle - (\sqrt{3}/2) \Delta \alpha_B \langle E_{02}^{(2)} \rangle] \\ &\approx (N/V) \Delta \alpha_U \langle E_{00}^{(2)} \rangle, \end{aligned} \quad (34)$$

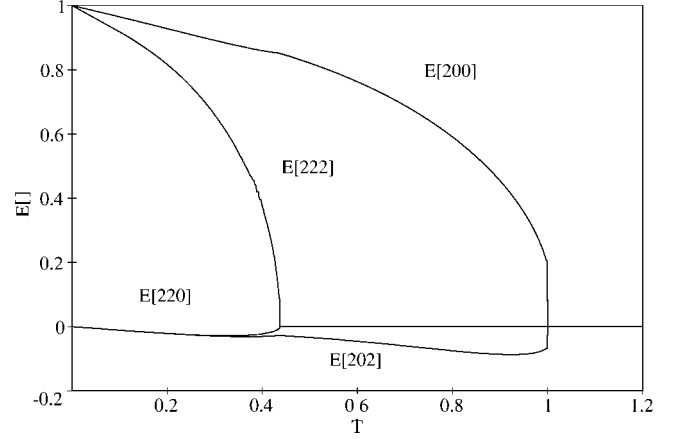


FIG. 1. The temperature dependence of the order parameters $\langle E_{\mu\nu}^{(j)} \rangle$ ($E[j\mu\nu]$ in the picture). T denotes the dimensionless temperature. The $I-N_U$ transition is at $T=1.0$ and the N_U-N_B transition is at $T=0.437$.

$$\begin{aligned} \Delta \chi_B &= (N/V) [\Delta \alpha_B \langle E_{22}^{(2)} \rangle - (2\sqrt{3}/3) \Delta \alpha_U \langle E_{20}^{(2)} \rangle] \\ &\approx (N/V) \Delta \alpha_B \langle E_{22}^{(2)} \rangle. \end{aligned} \quad (35)$$

We do not use the small density limit in our exemplary calculations.

IV. EXEMPLARY CALCULATIONS

In this section we carry out calculations for the system of biaxial molecules. We assume that the molecules are similar to ellipsoids with the three different axes $(2a) \times (2b) \times (2c)$, where $a:b:c$ is 1:2:5. The volume of every molecule is equal to $V_{mol} = (4/3)\pi abc$. We used the packing fraction $\rho = V_{mol} N/V = 0.1$; the density is constant. The elements of the polarizability tensor α and the shape factors are

$$\alpha_1 = 3V_{mol}, \quad \alpha_2 = 4V_{mol}, \quad \alpha_3 = 5.56722V_{mol}, \quad (36)$$

$$\Omega_1 = 0.95420, \quad \Omega_2 = 0.30760, \quad \Omega_3 = 0.05268. \quad (37)$$

The values of the polarizability tensor α come from the simple model described in Appendix C.

In order to get the values of the coefficients $v_{\mu\nu}^{(j)}$, we used the excluded volume method by Straley [8]. In our system, on decreasing the temperature, we meet the first-order transition from the isotropic to the uniaxial nematic phase ($I-N_U$) at $T_U=1.0$ (T denotes the dimensionless temperature) and the second-order transition to the biaxial nematic phase (N_U-N_B) at $T_B=0.437$. At the $I-N_U$ transition we have

$$\beta_U v_{00}^{(2)} = -3.99056,$$

$$\beta_U v_{02}^{(2)} = \beta_U v_{20}^{(2)} = 2.06457,$$

$$\beta_U v_{22}^{(2)} = -0.77740. \quad (38)$$

For an arbitrary temperature T we can calculate

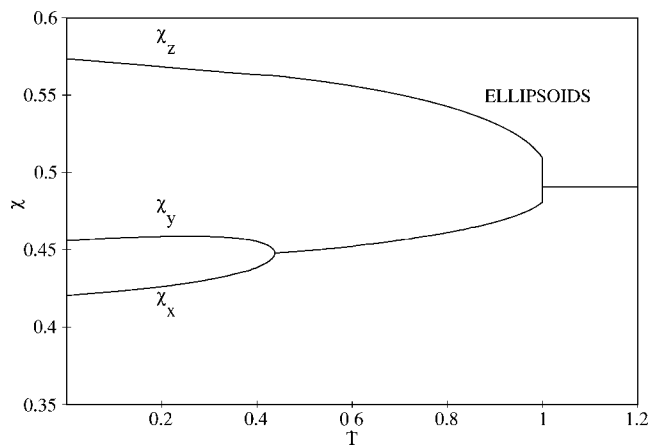


FIG. 2. The temperature dependence of the susceptibilities in the case of ellipsoids of dimensions 1:2:5. T denotes the dimensionless temperature. In the isotropic phase ($T > 1.0$) $\chi_x = \chi_y = \chi_z$. In the uniaxial nematic phase ($0.437 < T < 1.0$) we have $\chi_x = \chi_y < \chi_z$. In the biaxial nematic phase ($T < 0.437$) we get three independent $\chi_x < \chi_y < \chi_z$.

$$\beta v_{\mu\nu}^{(j)} = \beta_U v_{\mu\nu}^{(j)} T_U / T. \quad (39)$$

The temperature dependence of the order parameters $\langle E_{00}^{(2)} \rangle$, $\langle E_{02}^{(2)} \rangle$, $\langle E_{20}^{(2)} \rangle$, and $\langle E_{22}^{(2)} \rangle$ is presented in Fig. 1. The order parameters were used to calculate the temperature dependence of the susceptibility shown in Fig. 2.

In the uniaxial nematic phase we have $\chi_z > \chi_y = \chi_x$. At the N_U - N_B transition the lower susceptibility branch splits into two independent $\chi_y > \chi_x$. The results stay similar also in the case of rectangular boxes.

We would like to note that during numerical calculations one physical configuration can give several sets of different values of the order parameters. This is possible due to freedom of choice of the reference frame orientation. Let us consider the ideal biaxial nematic phase. There are six physically equivalent configurations where the symmetry axes coincide with the reference frame axes. They are summarized in Table I. We used the configuration with $(\vec{L}, \vec{M}, \vec{N}) = (\vec{e}_x, \vec{e}_y, \vec{e}_z)$ where the order parameters have the simplest values.

In our model we examined also the density dependence of the order parameters and of the susceptibility on the density

TABLE I. Physically equivalent configurations of the ideal biaxial nematic phase. We used the configuration with $(\vec{L}, \vec{M}, \vec{N}) = (\vec{e}_x, \vec{e}_y, \vec{e}_z)$.

LMN	$\langle E_{00}^{(2)} \rangle$	$\langle E_{02}^{(2)} \rangle$	$\langle E_{20}^{(2)} \rangle$	$\langle E_{22}^{(2)} \rangle$
XYZ	1	0	0	1
XZY	-1/2	$-\sqrt{3}/2$	$-\sqrt{3}/2$	1/2
YXZ	1	0	0	-1
YZX	-1/2	$-\sqrt{3}/2$	$\sqrt{3}/2$	-1/2
ZXY	-1/2	$\sqrt{3}/2$	$-\sqrt{3}/2$	-1/2
ZYX	-1/2	$\sqrt{3}/2$	$\sqrt{3}/2$	1/2

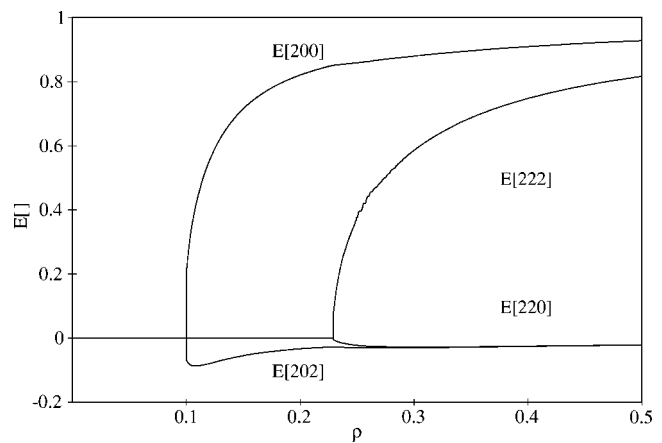


FIG. 3. The density dependence of the order parameters $\langle E_{\mu\nu}^{(j)} \rangle$ ($E[j\mu\nu]$ in the picture). ρ denotes the packing factor. The I - N_U transition is at $\rho = 0.1$ and the N_U - N_B transition is at $\rho = 0.229$.

at constant temperature. We assumed that the interactions are proportional to the phase density. The similar assumption was used in the context of the scaled particle theory by Cotter [36] and others. At constant temperature we get the following relation between the interaction coefficients:

$$\beta v_{\mu\nu}^{(j)}(\rho) = \beta v_{\mu\nu}^{(j)}(\rho_0) \rho / \rho_0, \quad (40)$$

where ρ_0 is the reference state density. We used $\rho_0 = 0.1$ and $\beta v_{\mu\nu}^{(j)}(\rho_0) = \beta_U v_{\mu\nu}^{(j)}(\rho_0)$ corresponding to the I - N_U transition ($T = T_U$). The density dependence of the order parameters is shown in Fig. 3. On increasing the density, we find the I - N_U transition at $\rho = 0.1$ and the N_U - N_B transition at $\rho = 0.229$. The density dependence of the susceptibilities in the case of ellipsoids is presented in Fig. 4.

We would like to note that for high densities the presented theory may be inadequate. As an approximate border for the

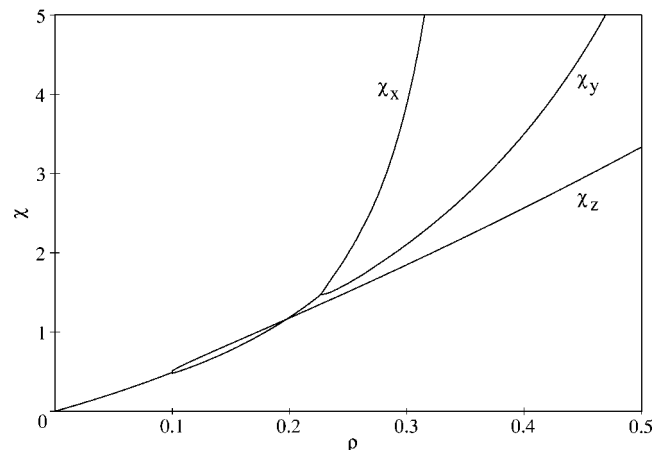


FIG. 4. The density dependence of the susceptibilities in the case of ellipsoids of dimensions 1:2:5. ρ denotes the packing factor. In the isotropic phase ($\rho < 0.1$) $\chi_x = \chi_y = \chi_z$. In the uniaxial nematic phase ($0.1 < \rho < 0.229$) we have $\chi_x = \chi_y < \chi_z$ and next $\chi_x = \chi_y > \chi_z$. In the biaxial nematic phase ($\rho > 0.229$) we get the relation $\chi_x > \chi_y > \chi_z$.

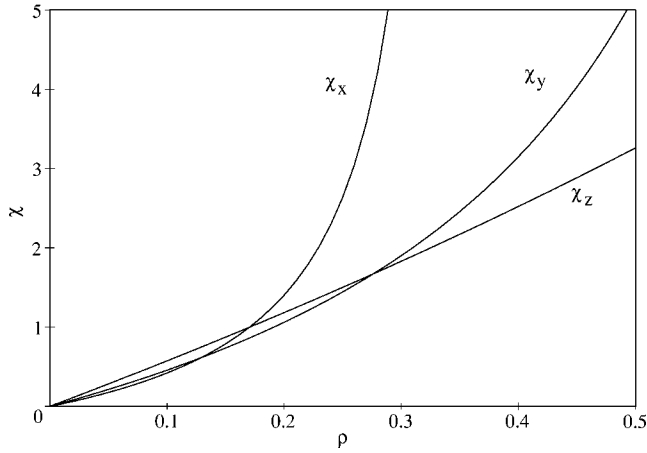


FIG. 5. The density dependence of the susceptibilities in the ideal biaxial phase (ellipsoids 1:2:5). ρ denote the packing factor. On increasing the density, we observe the ordering reversal of the susceptibilities from $\chi_x < \chi_y < \chi_z$ to $\chi_x > \chi_y > \chi_z$.

considered molecules we can choose $\rho=0.381$, where the negative susceptibilities appear.

In order to understand the susceptibility behavior we can write Eq. (29) in the case of the completely ordered phase ($\langle E_{00}^{(2)} \rangle = \langle E_{22}^{(2)} \rangle = 1$)

$$\chi_\lambda = \frac{(N/V)\alpha_\lambda}{1 - (N/V)\alpha_\lambda\Omega_\lambda}, \quad \lambda = x, y, z. \quad (41)$$

In our calculations we have $\alpha_1 < \alpha_2 < \alpha_3$ and $\alpha_1\Omega_1 > \alpha_2\Omega_2 > \alpha_3\Omega_3$. Thus, on increasing the density, we get the following sequence of relations (see Fig. 5):

$$\chi_x < \chi_y < \chi_z,$$

$$\chi_y < \chi_x < \chi_z,$$

$$\chi_y < \chi_z < \chi_x,$$

$$\chi_z < \chi_y < \chi_x.$$

But, in the isotropic and the uniaxial nematic phases, the selected order parameters are equal to zero, the corresponding susceptibilities can be identical, and the full sequence is not observed. We note that the full sequence can be obtained for the molecules at the so-called self-dual point ($ac=b^2$), where the direct $I-N_B$ transition appears.

V. SUMMARY

In the present paper we proposed a statistical theory of the dielectric susceptibility of nonpolar biaxial nematic liquid crystals. A generalized Clausius-Mossotti approach was used and the reaction field was neglected. We took into account the shape anisotropy of the molecules (biaxial molecules in biaxial cavity), the anisotropy of the phase (anisotropic and not averaged susceptibility in expressions), and the incomplete ordering (order parameters).

The biaxial molecules required complex expressions depending on the three Euler angles. In order to simplify cal-

culations, we defined a set of basic functions and have determined their properties.

The ordering of the phase was described by means of the mean field theory. We would like to note that this part of the theory is, to a certain degree, independent of the calculations of the susceptibilities and can be easily replaced by a more sophisticated approach.

The theory was used to calculate the temperature and the density dependence of the order parameters and of the susceptibilities for the model system. On decreasing the temperature at constant density, the splitting of the susceptibility was found to two and three branches at the isotropic-uniaxial nematic and uniaxial-biaxial nematic transitions, respectively. On increasing the density at constant temperature, splittings of the susceptibility were also found, but the ordering reversal of the susceptibilities was also present.

In conclusion, we note some possible extensions of the present theory. First, the theory should be extended to polar molecules. Early results for the uniaxial molecules are given in [4]. Recently, Mettout *et al.* [37] presented a theory of polar biaxial nematic phases based on the Landau expansion of the free energy. Second, the more realistic calculations of the polarizabilities are needed, which will be related to the data on the molecular structure. Finally, one should consider also spatially ordered phases (smectic, crystalline) which can appear instead of the biaxial nematic phase.

APPENDIX A

Below we list the properties of the functions $E_{\mu\nu}^{(j)}$. The functions can be used to describe any physical quantity that depends on the three Euler angles.

(1) The definition is

$$E_{\mu\nu}^{(j)}(R) = \text{norm}(\mu, \nu) \times [D_{\mu\nu}^{(j)}(R) + \text{sgn}(\mu)\text{sgn}(\nu)(-1)^{\mu+\nu} \times D_{-\mu, -\nu}^{(j)}(R) + \text{sgn}(\nu)(-1)^\nu D_{\mu, -\nu}^{(j)}(R) + \text{sgn}(\mu) \times (-1)^\mu D_{-\mu, \nu}^{(j)}(R)],$$

where $R=(\phi, \theta, \psi)$ (the three Euler angles), j is a non-negative integer, and μ and ν are integers. The functions $D_{\mu\nu}^{(j)}$ are the standard rotation matrix elements [35] and

$$\text{norm}(x, y) = \left(\frac{1}{\sqrt{2}} \right)^{2+\delta_{0x}+\delta_{0y}} \frac{1}{2} [(1+i) + (1-i)\text{sgn}(x)\text{sgn}(y)],$$

$$\text{sgn}(x) = \begin{cases} 1 & \text{for } x \geq 0, \\ -1 & \text{for } x < 0. \end{cases}$$

Note that

$$\text{sgn}(-x) = -\text{sgn}(x) + 2\delta_{0x}.$$

We have also

$$\left\{ \frac{1}{2} [(1+i) + (1-i)\text{sgn}(\mu)\text{sgn}(\nu)] \right\}^2 = \text{sgn}(\mu)\text{sgn}(\nu).$$

(2) The functions $E_{\mu\nu}^{(j)}$ are real.

(3) For any j the number of the functions $E_{\mu\nu}^{(j)}$ equals $(2j+1)^2$ and it is also the number of functions $D_{\mu\nu}^{(j)}$.

(4) The functions satisfy the orthogonality relation

$$\int dR E_{\mu\nu}^{(j)}(R) E_{\rho\sigma}^{(k)}(R) = \delta_{jk} \delta_{\mu\rho} \delta_{\nu\sigma} 8\pi^2 / (2j+1).$$

We can write more generally

$$\int dR E_{\mu\nu}^{(j)}(R) E_{\rho\sigma}^{(k)}(R_1^{-1}R) = \frac{8\pi^2}{2j+1} \delta_{jk} E_{\mu\rho}^{(j)}(R_1) \delta_{\nu\sigma} \frac{1}{2} [1 - \text{sgn}(\mu)\text{sgn}(\nu) + \text{sgn}(\rho)\text{sgn}(\nu) + \text{sgn}(\mu)\text{sgn}(\rho)].$$

(5) The properties connected with the physical system symmetries are

$$E_{\mu\nu}^{(j)}(RR_z(\pi)) = (-1)^\nu E_{\mu\nu}^{(j)}(R),$$

$$E_{\mu\nu}^{(j)}(R_z(\pi)R) = (-1)^\mu E_{\mu\nu}^{(j)}(R),$$

$$E_{\mu\nu}^{(j)}(RR_y(\pi)) = \text{sgn}(\nu)(-1)^j E_{\mu\nu}^{(j)}(R),$$

$$E_{\mu\nu}^{(j)}(R_y(\pi)R) = \text{sgn}(\mu)(-1)^j E_{\mu\nu}^{(j)}(R).$$

(6) Let $R^{-1} = (-\psi, -\theta, -\phi)$ denote the rotation inverse to $R = (\phi, \theta, \psi)$. Then

$$E_{\mu\nu}^{(j)}(R^{-1}) = \text{sgn}(\mu)\text{sgn}(\nu) E_{\nu\mu}^{(j)}(R).$$

(7) For the zero rotation ($\phi = \theta = \psi = 0$) we have

$$E_{\mu\nu}^{(j)}(0) = \delta_{\mu\nu}.$$

(8) The connections between the functions $E_{\mu\nu}^{(j)}$ and the invariants $F_{\mu\nu}^{(j)}$ [26] are as follows. For j, μ, ν even and $\mu, \nu \geq 0$

$$F_{\mu\nu}^{(j)} = E_{\mu\nu}^{(j)}.$$

For j odd, μ, ν even, and $\mu, \nu \geq 2$

$$F_{\mu\nu}^{(j)} = E_{-\mu-\nu}^{(j)}.$$

(9) Let us assume that the three Euler angles $R = (\phi, \theta, \psi)$ determine the orientation of the three unit orthogonal vectors $(\vec{l}, \vec{m}, \vec{n})$. The vector coordinates can be expressed by means of the functions $E_{\mu\nu}^{(1)}$:

$$l_x = E_{11}^{(1)}(R) = \cos \theta \cos \phi \cos \psi - \sin \phi \sin \psi,$$

$$l_y = -E_{-11}^{(1)}(R) = \cos \theta \sin \phi \cos \psi + \cos \phi \sin \psi,$$

$$l_z = E_{01}^{(1)}(R) = -\sin \theta \cos \psi,$$

$$m_x = E_{1-1}^{(1)}(R) = -\cos \theta \cos \phi \sin \psi - \sin \phi \cos \psi,$$

$$m_y = E_{-1-1}^{(1)}(R) = -\cos \theta \sin \phi \sin \psi + \cos \phi \cos \psi,$$

$$m_z = E_{0-1}^{(1)}(R) = \sin \theta \sin \psi,$$

$$n_x = E_{10}^{(1)}(R) = \sin \theta \cos \phi,$$

$$n_y = -E_{-10}^{(1)}(R) = \sin \theta \sin \phi,$$

$$n_z = E_{00}^{(1)}(R) = \cos \theta.$$

(10) The integral over the product of three $E_{\mu\nu}^{(j)}$ has the form

$$\begin{aligned} \int dR E_{\mu_1\nu_1}^{(j_1)}(R) E_{\mu_2\nu_2}^{(j_2)}(R) E_{\mu_3\nu_3}^{(j_3)}(R) &= 8\pi^2 \text{norm}(\mu_1, \nu_1) \text{norm}(\mu_2, \nu_2) \text{norm}(\mu_3, \nu_3) [1 + \text{sgn}(\mu_1)\text{sgn}(\mu_2)\text{sgn}(\mu_3)(-1)^{(j_1+j_2+j_3)}] \\ &\times [1 + \text{sgn}(\nu_1)\text{sgn}(\nu_2)\text{sgn}(\nu_3)(-1)^{(j_1+j_2+j_3)}] \left[\begin{pmatrix} j_1 & j_2 & j_3 \\ \mu_1 & \mu_2 & \mu_3 \end{pmatrix} + \begin{pmatrix} j_1 & j_2 & j_3 \\ -\mu_1 & \mu_2 & \mu_3 \end{pmatrix} \right] \\ &\times (-1)^{\mu_1} \text{sgn}(\mu_1) + \begin{pmatrix} j_1 & j_2 & j_3 \\ \mu_1 & -\mu_2 & \mu_3 \end{pmatrix} (-1)^{\mu_2} \text{sgn}(\mu_2) + \begin{pmatrix} j_1 & j_2 & j_3 \\ \mu_1 & \mu_2 & -\mu_3 \end{pmatrix} (-1)^{\mu_3} \text{sgn}(\mu_3) \\ &\times \left[\begin{pmatrix} j_1 & j_2 & j_3 \\ \nu_1 & \nu_2 & \nu_3 \end{pmatrix} + \begin{pmatrix} j_1 & j_2 & j_3 \\ -\nu_1 & \nu_2 & \nu_3 \end{pmatrix} (-1)^{\nu_1} \text{sgn}(\nu_1) + \begin{pmatrix} j_1 & j_2 & j_3 \\ \nu_1 & -\nu_2 & \nu_3 \end{pmatrix} (-1)^{\nu_2} \text{sgn}(\nu_2) \right. \\ &\left. + \begin{pmatrix} j_1 & j_2 & j_3 \\ \nu_1 & \nu_2 & -\nu_3 \end{pmatrix} (-1)^{\nu_3} \text{sgn}(\nu_3) \right], \end{aligned}$$

where $\begin{pmatrix} j & k & l \\ \mu & \nu & \rho \end{pmatrix}$ are the 3- j symbols of Wigner [35]. As a special case ($j_3 = \mu_3 = \nu_3 = 0$), we can obtain the orthogonality equation.

APPENDIX B

In our approach we assume that a molecule is in the non-spherical cavity of molecular dimensions and surrounded by

the anisotropic continuum. The cavity shape is taken into account when we calculate the dependence of the internal electric field on the macroscopic electric field and on the polarization. As a result we get different shape factors for different possible shapes.

(1) The shape factors for the ellipsoids with the axes $2a \times 2b \times 2c$ are

$$\Omega_1 = J(1 - a^2/b^2, 1 - a^2/c^2),$$

$$\Omega_2 = J(1 - b^2/a^2, 1 - b^2/c^2),$$

$$\Omega_3 = J(1 - c^2/a^2, 1 - c^2/b^2),$$

where the function $J(x, y)$ we define for $x < 1$ and $y < 1$ as

$$J(x, y) = \int_0^1 \frac{dt t^2}{\sqrt{(1 - x t^2)(1 - y t^2)}}.$$

Generally, the function $J(x, y)$ can be expressed by means of the elliptic integrals, but in special cases (uniaxial molecules) there are simple results. For $w > 0$ we have

$$J(x, y) = J(y, x),$$

$$J(0, 0) = \frac{1}{3},$$

$$J(w^2, 0) = \frac{1}{2w^3} [\arcsin(w) - w\sqrt{1 - w^2}],$$

$$J(-w^2, 0) = \frac{1}{2w^3} [w\sqrt{1 + w^2} - \ln|w + \sqrt{1 + w^2}|],$$

$$J(w^2, w^2) = \frac{1}{w^3} [-w + \operatorname{arctanh}(w)],$$

$$J(-w^2, -w^2) = \frac{1}{w^3} [w - \operatorname{arctan}(w)].$$

(2) The shape factors for the rectangular boxes of dimensions $2a \times 2b \times 2c$ are

$$\Omega_1 = \frac{2}{\pi} \arcsin \left[\frac{bc}{\sqrt{(a^2 + b^2)(a^2 + c^2)}} \right],$$

$$\Omega_2 = \frac{2}{\pi} \arcsin \left[\frac{ac}{\sqrt{(a^2 + b^2)(b^2 + c^2)}} \right],$$

$$\Omega_3 = \frac{2}{\pi} \arcsin \left[\frac{ab}{\sqrt{(a^2 + c^2)(b^2 + c^2)}} \right].$$

Note that $\Omega_1 + \Omega_2 + \Omega_3 = 1$.

APPENDIX C

Let us explain the values of the polarizability tensor α . We considered a simple model of a molecule as a set of parallel chains of atoms. For a molecule of dimensions 1:2:5 we have two chains, which consist of five atoms (or five chains with two atoms). One atom consists of the pointlike positive charge and the spherical cloud of the negative charge. The relative positions of the positive charges are fixed whereas the negative charge positions can change. In the absence of the electric field, the negative charge centers coincide with the positive charges.

Let us consider a chain of n atoms. When a *weak* electric field \vec{E} is applied *along* the chain, the negative charge centers do not coincide with the positive charges and dipole moments are induced. We assume that the positive and negative charges interact with one another and with the external field. The chain volume V_{chain} is the sum of the atom volumes. The induced polarizability along the chain α_{chain} we define as

$$\vec{p} = \alpha_{chain} \epsilon_0 \vec{E}$$

and it has the dimension of the volume. We calculated the total dipole moments and the induced polarizability for different chain lengths n :

$$n = 1, \quad \alpha_{chain} = 3V_{chain},$$

$$n = 2, \quad \alpha_{chain} = 4V_{chain},$$

$$n = 3, \quad \alpha_{chain} = 4.703\ 70V_{chain},$$

$$n = 4, \quad \alpha_{chain} = 5.203\ 46V_{chain},$$

$$n = 5, \quad \alpha_{chain} = 5.567\ 22V_{chain},$$

$$n = 6, \quad \alpha_{chain} = 5.839\ 51V_{chain},$$

$$n = 7, \quad \alpha_{chain} = 6.048\ 90V_{chain},$$

$$n = 8, \quad \alpha_{chain} = 6.213\ 89V_{chain},$$

$$n = 9, \quad \alpha_{chain} = 6.346\ 70V_{chain}. \quad (C1)$$

The induced polarizability values calculated for the chains were used as an approximation of the molecule polarizabilities in different directions (V_{chain} was replaced with V_{mol}).

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