Tetrahedral symmetry in nematic liquid crystals

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By means of symmetry consideration the order parameter U_{ijk} of a tetrahedral nematic liquid crystal (LC) was derived. In contrast to other nematic LC's (including uniaxial, biaxial, cubic, and icosahedral phases) the odd rank (=3) of U_{ijk} permits the phase transition of both the first and second order from isotropic liquid into tetrahedral nematic LC's and leads to the appearance of one of two possible helical structures in the chiral T phase of this nematic LC. In the framework of the mean-field approximation the contribution of the orientational part of the LC order parameter to the polarizability of LC with different symmetries was found and the existence of the second order phase transition from isotropic liquid into nonchiral tetrahedral nematic LC's has been predicted. The Fréedericksz transition in the nonchiral T_d phase was considered: the peculiarities of the bifurcation tree crucially depended on the direction of the external field with respect to the rotational C_3 and screw $\bar{C}_4$ axes of the unperturbed tetrahedral phase. The untwisting and deviation of the helical T phase in external fields were discussed. The structure of the disclination core in a tetrahedral nematic LC was analyzed.

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I. INTRODUCTION

The absence of translational symmetry in the nematic phase of liquid crystals (LC's) admits the point symmetry groups–subgroups of O(3), including the groups forbidden in crystalline lattice. The existence of nonuniaxial nematic phases was predicted [1,2] long before they were found in the lyotropic mesophase [3]. After that by means of traditional conoscopic and calorimetric techniques as well as the NMR and x-ray diffraction there were identified many nonuniaxial phases in thermotropic nematic (LC's): monoclinic [4,5], rhombic [6,7], tetragonal [8] and cubic [9]. In the paper [10] the properties of the hypothetical icosahedral nematic LC's were described. In a lyotropic LC, rhombohedral, tetragonal, and cubic phases were also observed [11].

This variety of nematic LC of different point symmetry groups G initiated development of the theory of physical phenomena (elasticity, flexoelectricity, hydrodynamics) for a nematic LC of arbitrary symmetry [12–15]. The theory of linear defects for the most groups G was developed in the framework of a homotopical approach [16]. The orientational order parameter Q_w which was used in the Landau-de Gennes theory of a nematic LC is well known for middle (w=2) crystallographic point groups D_k, D_{kd}, and D_{kh} where w is the rank of the symmetric traceless tensor. For higher symmetries, it was constructed in [17–19] for cubic groups (w=4) and in [20–23] for icosahedral groups (w=6). Tetrahedral nematic LC's which correspond to w=3 have not been discussed previously. One reason for this is that they have not been observed experimentally until now. Another reason is that the main problems of LC theory were solved in the 1970's and 1980's and the gradual decrease of interest to this branch of condensed matter in the last decade has left a number of unresolved questions.

In the theory of condensed matter, the tetrahedral symmetry was successfully used to describe defects in disordered phases (metallic glasses, Caspar-Frank phases) as frustrations of tetrahedral packing [24]. The tetrahedral symmetry of a nematic LC also could be a source of disclination lines [16]. In contrast to other nematic LC's the odd rank of Q_3 permits the phase transition of both the first and second order from isotropic liquid into tetrahedral nematic. Moreover, the framework of the mean-field approximation leads only to the second order phase transition. Another consequence of this is that the Fréedericksz transition in tetrahedral LC phases depends on the sign of the applied field (opposite directions of a field of the same magnitude must give different deviation planes for the tetrahedral bonds).

The continual theory of tetrahedral nematic LC's in the framework of the Ericksen-Leslie theory was discussed in papers [14,15]. Our objective here is to derive the order parameter Q_3 of a tetrahedral nematic LC and to develop on its ground the theories of phase transition from an isotropic liquid into a tetrahedral nematic LC and orientational Fréedericksz transition. Next, an equilibrium state of a chiral phase free from the applied fields and in the presence of such fields will be discussed. The core of disclination line in those phases will be considered.

II. SYMMETRY CONSIDERATIONS

We begin here with a brief summary of the symmetry properties of the order parameter Q_w for mesophases of different point groups G. The tetrahedral order parameter Q_3 will be found to flow naturally from these considerations. Symmetry classification of LC phases on

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the ground of four-particle correlation functions [25] has shown that the orientational order parameter Q of the LC phase can be constructed by means of the components of the irreducible tensor λ_w of integer rank w. However the symmetry of LC point group G could reduce the number Z of independent scalar invariants $I_w(G)$ of tensor Q_w, moreover it could make Z equal to zero, e.g., for Q_2

$$Z[I_2(D_{2h})] = 2, \quad Z[I_2(D_{4h})] = 1, \quad Z[I_2(O_h)] = 0.$$

Therefore, the orientational order parameter Q of a LC for the certain point group G might be naturally chosen as the first nonvanishing symmetric traceless tensor Q_w which satisfies the following conditions:

$$Z[I_w(G)] \neq 0, \quad Z[I_v(G)] = 0\ , \ v = 1, 2, ..., w-1. \qquad (1)$$

Now for LC phases not possessing the inversion center or reflection planes, we should take into account an opportunity to construct pseudoscalar invariants by means of the terms $Q_w \nabla Q_w$ (chiral phase). Thus it is not difficult to realize [26] that for subgroups G of the three-dimensional orthogonal group O(3) a sequence of order parameters Q_w is finite and well defined. In Table I, q_0 and q_m, u, r, s are the modules of tensor order parameters Q_2, Q_3, Q_4, Q_6, respectively. For construction of tensors Q_w we have used M unitary vectors $\mathbf{n}^m$: if $w = 2$ these vectors are directed along three rotational axes C_2 of rectangular parallelepiped; if $w = 3$, along four rotational axes C_3 of tetrahedron; if $w = 4$, along three rotational axes C_2 of tetrahedron or C_4 of cube; if $w = 6$, along 15 rotational axes C_2 of icosahedron. Six Greek indices $\alpha, \beta, ..., \nu$ in the expression for Q_6 take all noncoinciding values of six Latin indices $i, j, ..., t$. The expression for Q_3 can be obtained by summation over m of four irreducible tensors of the third rank $\lambda_3^m = u\ [\ n_i^m n_j^m n_k^m - 1/5\ (n_i^m \delta_{jk} + n_j^m \delta_{ik} + n_k^m \delta_{ij})]$.

The obtained list of order parameters Q_w exhausts all possible nematic LC phases. As presumed, it corresponds to the list of finite subgroups of group SO(3) : C_k ($k \geq 1$), D_k ($k \geq 2$), T, O, Y.

III. TETRAHEDRAL NEMATIC PHASE

From all nematic phases (see Table I) the tetrahedral phase is the only one that has an antisymmetric order parameter $Q_3 = U_{ijk}$ with respect to inversion of vectors $\mathbf{n}^m$

$$U_{ijk}(-\mathbf{n}) = -U_{ijk}(\mathbf{n}). \qquad (2)$$

It leads to some peculiarities of the physical properties of those phases.

A. Phase transition

The phase transition from isotropic liquid into nonchiral phase T_d of a tetrahedral nematic LC can occur as a transition of both the first or the second order in contrast to a weak phase transition of only the first order into other nematic phases (with the exception of the second order phase transition in a tricritical point [2]). It follows from the fact that the rank of tensor U_{ijk} is odd. Therefore, one can construct the scalar invariants only

TABLE I. Mesophases: Symmetry groups and orientational order parameters. [Continuing the tradition that was given rise to by Schouten [27] (Q_2–*deviator*–5, Q_3–*septor*–7, Q_4–*nonor*–9) an irreducible tensor Q_6 might be called, in the Latin manner, *tridecor* according to the number (13) of its independent components in the general case.]

w	Symmetry group G and orientational order parameter Q_w
0	Isotropic liquid G =SO(3) for chiral liquid, and O(3) for nonchiral liquid Q_0 = 0–scalar
1	Vector liquid $G = C_k$ for chiral, $G = C_{kv}$ for nonchiral polar, and $G = C_{kh}, S_k$ for nonchiral axial $Q_1 = \mathbf{n}$–unitary vector
2	Uniaxial nematic LC $G = D_{k+1}$, $k \geq 2$ for chiral (cholesteric), $G = D_{kd}, D_{(k+1)h}$, $k \geq 2$ for a nonchiral $Q_2 = q_0\ (n_i n_j - 1/3\ \delta_{ij})$–unitary deviator Biaxial nematic LC $G = D_2$ for chiral, $G = D_{2h}$ for nonchiral $Q_2 = \sum_{m=1}^{M=3} q_m (n_i^m n_j^m - 1/3\ \delta_{ij})$–deviator, $\sum_{m=1}^{M=3} q_m = 0$
3	Tetrahedral nematic LC $G = T$ for chiral, $G = T_d$ for nonchiral $Q_3 = u \sum_{m=1}^{M=4} n_i^m n_j^m n_k^m$–unitary septor
4	Cubic nematic LC $G = O$ for chiral, $G = T_h, O_h$ for nonchiral $Q_4 = r\ [\sum_{m=1}^{M=3} n_i^m n_j^m n_k^m n_l^m - 1/5\ (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})]$–unitary nonor
6	Icosahedral nematic LC $G = Y$ for chiral, $G = Y_h$ for nonchiral $Q_6 = s\ [\sum_{m=1}^{M=15} n_i^m n_j^m n_k^m n_l^m n_p^m n_t^m - 1/7 \sum_{(\ )=1}^{15} (\delta_{\alpha\beta}\delta_{\gamma\rho}\delta_{\mu\nu})]$–unitary $\cdots$

of even order: $U_{ijk}U_{kji}$, $(U_{ijk}U_{kji})^2$, etc. [Restricting ourselves by considering only the symmetric third rank tensor V_{ijk} we can build two independent scalars of the fourth order, $(V_{ijk})^4$, $V_{ijk}V_{klp}V_{lpq}V_{qij}$; three independent scalars of the sixth order, $(V_{ijk})^6$, $(V_{ijk})^3V_{klp}V_{lpq}V_{qij}$, $V_{ijk}V_{klp}V_{lpq}V_{qrs}V_{rst}V_{tij}$, etc. If the trace of V_{ijk} is zero, we have only one independent scalar in every sequence pointed above.] The density F of the free energy of the T_d nematic LC near the phase transition reads

$$F = a_1\, U_{ijk}U_{kji} + a_2\, (U_{ijk}U_{kji})^2 + a_3\, (U_{ijk}U_{kji})^3 + \cdots \,. \tag{3}$$

The T_d nematic phase forms a spatially homogeneous distribution of the tetrahedral bonds.

The phase transition from an isotropic liquid into the chiral phase T of a tetrahedral nematic LC also can be of both the first or the second order due to the considerations discussed above for the T_d phase. However, the appearance of the term $U_{ijk}\nabla U_{ijk}$ in (3), like other quadratic derivatives which described the elasticity, can lead to the spatially inhomogeneous ordering of the T phase as well as in ordinary cholesteric LC ($G = D_\infty$).

What kinds of space ordering does a chiral tetrahedral nematic LC form? This question can be considered in two versions. The first one is to find a phase diagram in parametric space [temperature-chirality-applied field (probably)] for a chiral liquid crystal with order parameter U_{ijk}. Obviously such a diagram would include the branches of the disorder phase (isotropic liquid) and the tetrahedral T phase. Besides, one can also suppose some more phases with an intricate space package similar to the blue phases in the narrow temperature region between uniaxially twisted phases and the disorder phase. This approach assumes an analysis of the full expression of free energy F_T including the gradient and nongradient terms (see the realization of such a program for blue phases in [28]).

The second version is more modest and, therefore, more restricted — to find a possible space ordering of the chiral tetrahedral nematic LC by considering only the gradient part of the free energy F_T. It means that we are far from the phase transition. This approach naturally does not say anything about the phase environment around the considered phase. The high symmetry of the chiral tetrahedral phase in comparison with the ordinary cholesteric LC shows that one can expect nontrivial solutions already at this stage. In the present paper, we restrict ourselves to the second version.

Let us choose for convenience another parametrization of tensor U_{ijk} by means of three unitary vectors $\mathbf{e}^i$ directed along rotational axes C_2 of the tetrahedral nematic LC (Fig. 1)

$$\mathbf{n}^1 = \frac{1}{\sqrt{3}}(\mathbf{e}^1 + \mathbf{e}^2 + \mathbf{e}^3),\quad \mathbf{n}^2 = \frac{1}{\sqrt{3}}(\mathbf{e}^1 - \mathbf{e}^2 - \mathbf{e}^3)\,,$$
$$\mathbf{n}^3 = \frac{1}{\sqrt{3}}(-\mathbf{e}^1 + \mathbf{e}^2 - \mathbf{e}^3),\quad \mathbf{n}^4 = \frac{1}{\sqrt{3}}(-\mathbf{e}^1 - \mathbf{e}^2 + \mathbf{e}^3)\,, \tag{4}$$

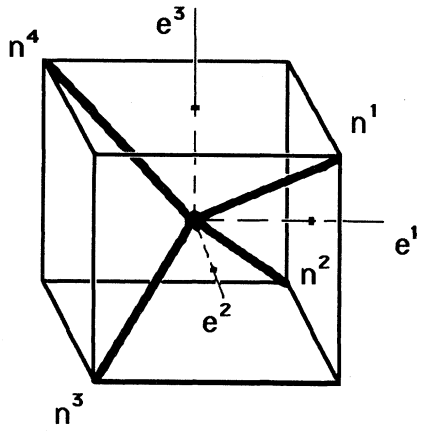

FIG. 1. Bonds in a tetrahedral nematic liquid crystal.

and conserving the conditions of the rigidity of tetrahedral bonds

$$\langle \mathbf{n}^i, \mathbf{n}^j \rangle = \tfrac{4}{3}\,(\,\delta^{ij} - \tfrac{1}{4}\,)\,. \tag{5}$$

The density F_T of the Frank free energy of a deformed T nematic LC with strong surface anchoring is described by four nonchiral K_i and one chiral ν elasticity modules, according to [14]

$$2F_T = \sum_{i=1}^{3} [\, K_1\, \mathrm{div}^2\, \mathbf{e}^i + K_2\langle \mathbf{e}^i, \mathrm{rote}^i\rangle^2 + \nu\langle \mathbf{e}^i, \mathrm{rote}^i\rangle] + K_3\,(\langle \mathbf{e}^2, \mathrm{rote}^1\rangle^2 + \langle \mathbf{e}^3, \mathrm{rote}^2\rangle^2 + \langle \mathbf{e}^1, \mathrm{rote}^3\rangle^2) + K_4\,(\langle \mathbf{e}^1, \mathrm{rote}^2\rangle^2 + \langle \mathbf{e}^2, \mathrm{rote}^3\rangle^2 + \langle \mathbf{e}^3, \mathrm{rote}^1\rangle^2)\,. \tag{6}$$

Notice that expression (6) is constructed on the grounds of nine independent pseudoscalars $\langle \mathbf{e}^i, \mathrm{rote}^j\rangle$. By means of vector identities for the right-hand triade $\mathbf{e}^1$, $\mathbf{e}^2$, $\mathbf{e}^3$

$$\mathrm{dive}^i = \langle \mathbf{e}^k, \mathrm{rote}^j\rangle - \langle \mathbf{e}^j, \mathrm{rote}^k\rangle,$$
$$(\mathbf{e}^i \times \mathrm{rote}^i)^2 = \langle \mathbf{e}^j, \mathrm{rote}^k\rangle^2 + \langle \mathbf{e}^k, \mathrm{rote}^j\rangle^2,\quad i \neq j \neq k$$

expression (6) can be represented as a quadratic form in nine-dimensional Euclidean space

$$2F_T = -3K_2\kappa^2 + \sum_{i=1}^{3}\Big[\, K_2(x_i + \kappa)^2 + \Big(K_1 + \frac{K_3 + K_4}{4}\Big)\, y_i^2 + \frac{K_3 - K_4}{2}\, y_i\, z_i + \frac{K_3 + K_4}{4}\, z_i^2\Big]\,, \tag{7}$$

where

$$\kappa = \frac{\nu}{2K_2}, \quad x_i = \langle \mathbf{e}^i, \mathrm{rot}\mathbf{e}^i \rangle, \quad y_i = \mathrm{div}\mathbf{e}^i,$$
$$z_i = \sqrt{2\,(\mathbf{e}^i \times \mathrm{rot}\mathbf{e}^i)^2 - \mathrm{div}^2\,\mathbf{e}^i}, \quad z_i^2 \geq 0\,. \tag{8}$$

The necessary conditions of positive definiteness of expression (7) are

$$K_2 > 0, \quad K_3 + K_4 > 0, \quad K_1 + \frac{K_3 + K_4}{4} > 0,$$
$$K_1 + \frac{K_3 K_4}{K_3 + K_4} > 0\,. \tag{9}$$

By satisfying these inequalities, the free energy F_T has an absolute minimum determined by the conditions

$$\mathrm{div}\mathbf{e}^i = 0, \quad (\mathbf{e}^i \times \mathrm{rot}\mathbf{e}^i)^2 = \mathbf{0}, \quad \langle \mathbf{e}^i, \mathrm{rot}\mathbf{e}^i \rangle + \kappa = \mathbf{0}\,. \tag{10}$$

It is easy to show that three scalar equations (10) for any vector $\mathbf{e}^i$ are equivalent to one vector equation with the nontrivial solution

$$\mathrm{rot}\mathbf{e}^i + \kappa\,\mathbf{e}^i = \mathbf{0}\,. \tag{11}$$

Thus we should have obtained a pure twist of each vector $\mathbf{e}^i$. Nevertheless, the rigidity conditions (5), which are valid in every point of three-dimensional space, forbid the *continuous* distribution of tetrahedral bonds with equal periodical twist of each vector $\mathbf{e}^i$. This can be proven by means of vector identities but we will point out a simple geometric argument. Indeed, a pure twist of two vectors, e.g., $\mathbf{e}^1$ and $\mathbf{e}^2$, gives rise to the twist axis Tw_3. It has a constant direction in the space and cannot coincide with third vector $\mathbf{e}^3$ because $\mathbf{e}^3$ itself is involved in the twist of the pairs $\mathbf{e}^3, \mathbf{e}^2$ and $\mathbf{e}^3, \mathbf{e}^1$. However this construction is forbidden in the three-dimensional space: $\mathbf{e}^3$ as the vector product of $\mathbf{e}^1$ and $\mathbf{e}^2$ must coincide with the twist axis Tw_3.

Making use of *continuous* functions we cannot provide the *absolute* minimum of the free energy F_T. In order to find a *continuous* distribution of tetrahedral bonds that minimizes *locally* (in vicinity of the equilibrium state) the expression (6) let us consider $\mathbf{e}^i(r)$ in the class of functions

$$\mathbf{N} = \mathrm{const}, \quad \mathbf{M}_i(r), \ \mathrm{rot}\mathbf{M}_i + \mu_i \mathbf{M}_i = \mathbf{0} \tag{12}$$

and put

$$\mathbf{e}^i = \alpha_i \mathbf{N} + \beta_i \mathbf{M}_i, \ \langle \mathbf{N}, \mathbf{M}_i \rangle = 0, \ N^2 = M_i^2 = 1\,. \tag{13}$$

Before we go on, it must be noticed that only one μ serves for three vectors $\mathbf{M}_i$; it could be proven by means of linear algebra. Now inserting (13) into expression (7) after simplifications we obtain

$$2F_T = -2K_2\kappa\mu B_2 + \left(K_2 - \frac{K_3 + K_4}{2}\right)\mu^2 B_4 + \frac{K_3 + K_4}{2}\mu^2 B_2\,, \tag{14}$$

where

$$B_2 = \sum_{i=1}^{3} \beta_i^2\,, \quad B_4 = \sum_{i=1}^{3} \beta_i^4\,.$$

One can find these sums by use of the two-parametric orientation of vectorial triade $\mathbf{M}_i$: $\alpha_i = \langle \mathbf{e}^i, \mathbf{N} \rangle = \cos\vartheta_i$, $i = 1, 2$. Then it is easy to show that

$$B_2 = 2\,, \quad B_4 = 2\,[\,1 + \Theta(\vartheta_1, \vartheta_2)]\,, \tag{15}$$

$$\Theta(\vartheta_1, \vartheta_2) = \cos^2\vartheta_1 \cos^2\vartheta_2 - \sin^2\vartheta_1 \cos^2\vartheta_1 - \sin^2\vartheta_2 \cos^2\vartheta_2\,.$$

Let us introduce the ratio between elasticity modules $\omega = (K_3 + K_4)/2K_2$. Minimizing the expression (14) with respect to μ one can find

$$\mu^* = \frac{\kappa}{1 + (1 - \omega)\,\Theta(\vartheta_1, \vartheta_2)}\,, \tag{16}$$

which leads to the free energy $F_T = -K_2\kappa\mu^*(\vartheta_1, \vartheta_2)$. Now the final step is to find the minimum of the free energy with respect to the angular variations of ϑ_1, ϑ_2. After a simple algebraic procedure we will get the following:

(i) a uniaxial phase with a helical axis along the rotational axis C_3 of chiral tetrahedral nematic [Fig. 2(a)]

$$0 \leq \omega < 1, \ \mu^*_{C_3} = \frac{3\kappa}{2 + \omega}, \ F_{C_3} = -\frac{3K_2\kappa^2}{2 + \omega}\,,$$
$$\vartheta_1^* = \vartheta_2^* = \arctan(\pm\sqrt{2})\,; \tag{17}$$

(ii) a uniaxial phase with a helical axis along the rotational axis C_2 of chiral tetrahedral nematic [Fig. 2(b)]

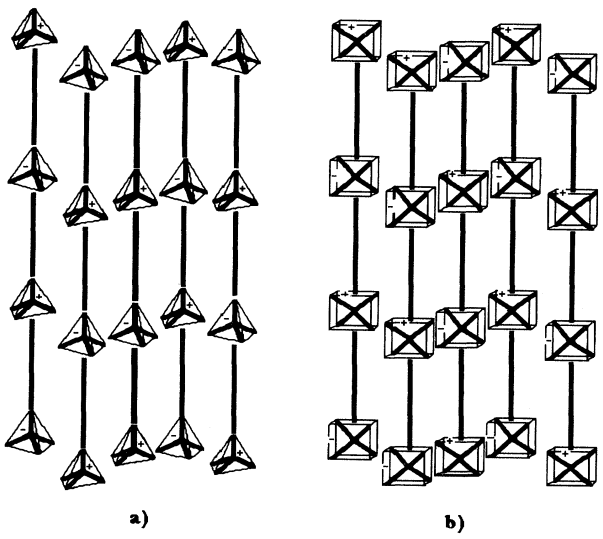

FIG. 2. Uniaxial chiral phases of a tetrahedral nematic LC: (a) C_3 helix, (b) C_2 helix.

$$\omega > 1,\ \ \mu^*_{C_2} = \kappa,\ \ F_{C_2} = -K_2\kappa^2,\ \ \vartheta^*_1 = 0,\ \vartheta^*_2 = \pi/2\ . \tag{18}$$

As follows from formulas (17) and (18), the pitch $h = 2\pi/\mu^*$ of a helical tetrahedral structure depends on the anisotropy of the LC elasticity only in case (i).

B. Polarization

A conclusion about the order of the phase transition could also be drawn in the framework of the mean-field approximation in statistical physics (see a modified variant of the Maier-Saupe theory in the Sec. III C). First of all, it is necessary to determine an angular order parameter for a tetrahedral nematic LC similarly as $\langle\cos\theta\rangle$ for a paramagnetic gas or as $\langle\cos^2\theta\rangle - 1/3$ for a uniaxial nematic LC [29]. In the present section we will restrict ourselves to the determination of such an angular parameter $\langle\Omega\rangle$ considering a polarization of a tetrahedral nematic LC.

Let us put a tetrahedral nematic LC in electric field $\mathbf{E}$. The density of energy of their interaction is

$$2W = -U_{ijk}E_iE_jE_k = -u\sum_{m=1}^{4}\langle\mathbf{n}^m,\mathbf{E}\rangle^3\ . \tag{19}$$

Then, in $\mathbf{e}^i$ basis we find

$$W = -\frac{4}{\sqrt{3}}\,u\,\langle\mathbf{e}^1,\mathbf{E}\rangle\,\langle\mathbf{e}^2,\mathbf{E}\rangle\,\langle\mathbf{e}^3,\mathbf{E}\rangle\ . \tag{20}$$

The one-particle distribution function of the tetrahedral bonds is $\rho(U) = a\exp(-W/kT)$, where a is the normalizing constant. Going over to the spherical coordinates we obtain

$$\rho(U) = a\exp\left(\frac{2}{\sqrt{3}}\,\frac{u}{kT}E^3\cos\theta\sin^2\theta\sin 2\varphi\right)\ . \tag{21}$$

The value $\langle\Omega\rangle = \langle\cos\theta\sin^2\theta\sin 2\varphi\rangle$ can be taken as the angular order parameter that goes to zero in the isotropic phase. Applying the general definition of $\langle\Omega\rangle$

$$\langle\Omega\rangle = \int_0^{\pi}\int_0^{2\pi}\Omega(\theta,\varphi)\rho(U)\sin\theta\ d\theta\ d\varphi\ , \tag{22}$$

let us present a final result omitting the details of the calculation procedure,

$$\langle\Omega\rangle = \frac{d}{d\gamma}\ \ln\left[\int_0^1 I_0(\gamma x(1-x^2))\ dx\right]\ , \tag{23}$$

where $\gamma = \frac{2}{\sqrt{3}}\,\frac{u}{kT}E^3$ and $I_0(x)$ is a modified Bessel function. It is easy to show that in the weak field ($\gamma < 1$)

$$\langle\Omega\rangle = \frac{4}{105}\,\gamma = \frac{8}{105\sqrt{3}}\,\frac{u}{kT}E^3\ . \tag{24}$$

Defining a polarization $\mathbf{P}$ of the nematic phase by the formula

$$\bar{W} = -\langle\mathbf{P},\mathbf{E}\rangle \tag{25}$$

and assuming that the contribution to $\bar{W} = \langle W\rangle$ from every tetrahedral bond is given by (20) we will find

$$\bar{W} = -\frac{2}{\sqrt{3}}\,u\,E^3\langle\Omega\rangle c\ ,$$

where c is the concentration of the tetrahedral bonds in the nematic phase. After inserting (24) into the last formula and comparing it with (25) we finally obtain

$$\mathbf{P} = p_3(E)\mathbf{E},\ \ p_3(E) = \frac{16}{315}\,\frac{u^2}{kT}\,c\,E^4\ , \tag{26}$$

where p_3 is the polarizability of the tetrahedral nematic LC.

It must be mentioned that the expression (26) could be simply generalized for any nematic phase (Table I): if an order parameter is a tensor Q_w of rank w with module b_w then the polarizability p_w of such a mesophase in the weak electric field ($b_wE^w < kT$) is

$$p_w \propto \frac{b_w^2}{kT}\,c\,E^{2(w-1)}\ .$$

In conclusion, we will make a remark: the last expression describes a contribution of an anisotropic part of the order parameter to the polarization of the nematic phase. There is really always an isotropic part of polarizability p_0 as a result of the induced dipole moment $p_0\mathbf{E}$. By analyzing the nonlinear contribution $E^{2(w-1)}$ to the polarizability of the nematic phase, one can determine a symmetry class w of liquid crystals according to Table I.

C. Maier-Saupe theory of tetrahedral nematic LC's

Consider now the phase transition from an isotropic liquid into a nonchiral phase T_d of the tetrahedral nematic LC in the framework of the mean-field approximation. Our approach is based on the Maier-Saupe theory for the uniaxial nematic LC's [29] with natural differences.

In accordance with this approximation a one-particle distribution function of the tetrahedral bonds is $\rho(U_i) = a\exp(-V_i/kT)$, where V_i is the orientational energy of the ith molecule in the mean molecular field $\langle\Omega\rangle$. Following the Maier-Saupe theory, we shall put $V_i \propto \langle\Omega\rangle$. Similarly, to the derivation of the orientational energy of the tetrahedral nematic LC's interaction with the electric field (19) and (20) we can obtain

$$V_i = -\bar{V}\ \langle\Omega\rangle\cos\theta_i\sin^2\theta_i\sin 2\varphi_i\ , \tag{27}$$

where $\bar{V}$ is an energetic constant which does not depend on temperature T. The spherical coordinates θ_i, φ_i describe the ith molecule position in the mean molecular field. It is natural to introduce a function

$$\Omega_i = \Omega(\theta_i,\varphi_i) = \cos\theta_i\sin^2\theta_i\sin 2\varphi_i \tag{28}$$

in order to construct a one-particle angular order parameter $\langle\Omega_i\rangle$ which goes to zero in the isotropic phase. According to the definition we have

$$\langle\Omega_i\rangle = \int_0^{\pi}\int_0^{2\pi} \Omega(\theta_i,\varphi_i)\ \rho(U_i)\sin\theta_i\ d\theta_i\ d\varphi_i\ , \tag{29}$$

where the one-particle distribution function $\rho(U_i)$ can be written as

$$\rho(U_i) = a\exp\left[\ \frac{\langle\Omega\rangle\bar{V}}{kT}\ \Omega(\theta_i,\varphi_i)\ \right]. \tag{30}$$

Now we are able to make the last step in the framework of the mean-field approximation and to postulate a self-consistent equation

$$\langle\Omega_i\rangle = \langle\Omega\rangle\ . \tag{31}$$

Inserting (28)–(30) into Eq. (31) after simple calculations we obtain

$$\frac{kT}{\bar{V}}v = \frac{d}{dv}[\ \ln\ \mathcal{Z}(v)\ ],$$
$$\mathcal{Z}(v) = \int_0^{\frac{\pi}{2}} I_0(v\sin t\cos^2 t)\ \cos t\ dt\ , \tag{32}$$

where $v = \frac{\bar{V}}{kT}\ \langle\Omega\rangle$. This nonlinear equation determines an implicit temperature dependence of the order parameter $\langle\Omega\rangle(T)$ as well as the temperature T^* of the phase transition where $\langle\Omega\rangle(T)\equiv 0$ if $T\geq T^*$.

Let us study analytically the behavior of $\langle\Omega\rangle(T)$ in the vicinity of the phase transition ($\langle\Omega\rangle \ll 1$). Using a power expansion for the modified Bessel function $I_0(x)$ and an integral representation for the β function $B(l,n)$ [30] one can find a statistical integral $\mathcal{Z}(v)$

$$\mathcal{Z}(v) = \sum_{l=0}^{\infty}\frac{b_l}{l!}\ v^{2l},\quad b_l = 2^l\frac{[(2l-1)!!]^2}{(6l+1)!!}\ , \tag{33}$$

where the first five coefficients b_l are

$$b_0 = 1,\ \ b_1 = \frac{2}{105}\cong 1.90\times 10^{-2}\ ,\ \ b_2\cong 2.66\times 10^{-4}\ ,$$
$$b_3\cong 2.75\times 10^{-6}\ ,\ \ b_4\cong 2.23\times 10^{-8}\ .$$

The logarithm of $\mathcal{Z}(v)$ can also be expanded in powers of v by means of a *cumulantial* expansion [31]

$$\ln\mathcal{Z}(v) = \sum_{l=1}^{\infty}\frac{c_l}{l!}\ v^{2l}\ , \tag{34}$$

where the so-called *cumulants* c_l are related to b_l in a regular manner

$$c_1 = b_1,\ c_2 = b_2 - b_1^2,\ c_3 = b_3 - 3b_1b_2 + 2b_1^3,$$
$$c_4 = b_4 - 4b_1b_3 - 3b_2^2 + 12b_1^2b_2 - 6b_1^4\ ,\ \cdots\ .$$

The first four of them are

$$c_1\cong 1.90\times 10^{-2}\ ,\ \ c_2\cong -0.96\times 10^{-4}\ ,$$
$$c_3\cong 1.35\times 10^{-6}\ ,\ \ c_4\cong -2.86\times 10^{-8}\ .$$

Finally, Eq. (32) gives

$$1 - \frac{T}{T^*} = d_1v^2 - d_2v^4 + d_3v^6 - ,\ \cdots\ ,$$

$$v = \frac{105}{4}\ \frac{T^*}{T}\ \langle\Omega\rangle\ , \tag{35}$$

$$d_1 = -\frac{c_2}{c_1}\cong 0.50\times 10^{-2},\ \ d_2 = \frac{c_3}{2c_1}\cong 0.34\times 10^{-4},$$
$$d_3 = -\frac{c_4}{6c_1}\cong 0.25\times 10^{-6}\ ,$$

where $T^* = 2c_1\frac{\bar{V}}{k} = \frac{4}{105}\frac{\bar{V}}{k}$ is a temperature of the second order phase transition. In the vicinity of T^* we immediately obtain from (35)

$$\langle\Omega\rangle(T) = \begin{cases} 2\sqrt{\frac{143}{1995}}\ (1-\frac{T}{T^*})^{\frac{1}{2}}\ , & T<T^* \\ 0\ , & T\geq T^*\ . \end{cases}$$

The numerical solution (Fig. 3) of the nonlinear equation (32) also confirms the conclusion about the order of the phase transition with ordinary dependence on the order parameter $\langle\Omega\rangle\propto\sqrt{T^*-T}$.

For the case $T\to 0$ we have

$$\langle\Omega\rangle\to\frac{2}{3\sqrt{3}}\cong 0.385\ ,$$

that also is in good agreement with numerical results (Fig. 3). This value comes from the maximization of $\Omega(\theta_i,\varphi_i)$ with respect to the angular coordinates θ_i,φ_i

$$\varphi_i = 45^\circ,\ \ \theta_i = \arccos\left(\frac{1}{\sqrt{3}}\right)\cong 54.7^\circ\ .$$

Let us finish this section with a short discussion of the influence of the thermal fluctuations of nematic bonds on the critical behavior of the nonchiral tetrahedral nematic LC in the vicinity of the phase transition into isotropic liquid. This question is obviously out of the scope of the mean-field approximation.

As was shown in [32] for the phase transition from a nonchiral uniaxial nematic LC into an isotropic liquid in the one-constant approximation we can operate with a model of three-component spins of the fixed length instead of the second rank traceless tensor Q_{ij} if the fluctuations of the module q of tensor order parameter Q_{ij} would have been neglected. In the framework of the above-mentioned approximations in [33], this approach was extended to the phase transition from a nonchiral biaxial nematic LC into an isotropic liquid: one can operate with a model of five-component spins of the fixed length instead of the second rank traceless tensor Q_{ij}. Following this approach, in our case we will use a model of seven-component spins of the fixed length (Appendix) instead of the third rank traceless tensor U_{ijk}. In this spin representation in accordance with power expansion (3) we have an isotropic model that belongs to the universality class $d=3$, $n=7$. This model has only one stable isotropic fixed point [34], where the second order

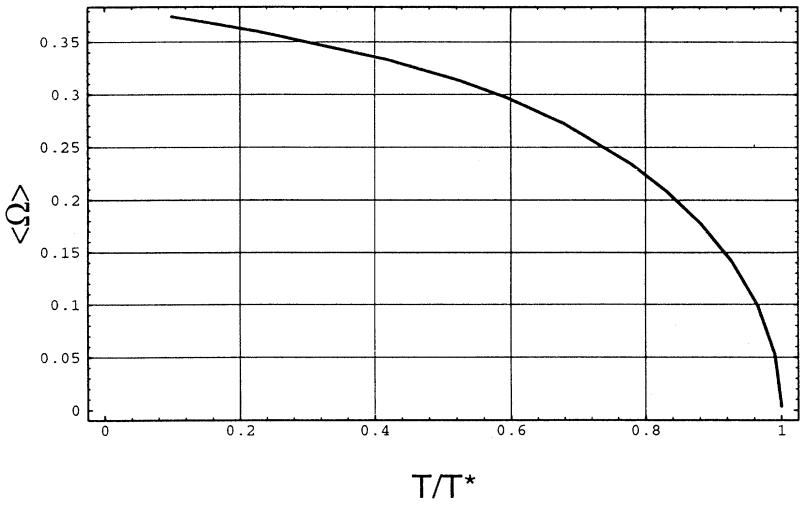

FIG. 3. Second order phase transition from isotropic liquid to the nonchiral tetrahedral nematic LC.

phase transition is valid at $T = T^*$. It is presumed here that the coefficient a_1 from the expansion (3) is defined as $a_1 = a_1^0(T - T^*)$. The critical indices in the small vicinity δT of this point T^* are determined by the ϵ expansion which in our case gives for the order parameter up to the power ϵ^2

$$\langle \Omega \rangle \propto (T^* - T)^\beta, \quad \beta = 0.42 \, .$$

The width δT of the critical temperature range is determined by the *Ginzburg* criterion.

D. Fréedericksz transition

In this chapter we will discuss the behavior of the nonchiral tetrahedral nematic LC contained in an infinite plane-parallel slab in electric field **E**. It presumes a strong anchoring of nematic bonds at the boundaries; an electric field is applied perpendicular to the boundary plane.

The free energy of the deformed T_d nematic LC in the **E** field calculated per unit area of the surface of the plane-parallel LC layer is described by the functional

$$J = \frac{1}{2L} \int_{-L}^{L} (F_{T_d} + W) \, dz \, , \tag{36}$$

where W was defined in (20), F_{T_d} is the density of the Frank free energy of the deformed T_d nematic LC [14]

$$2F_{T_d} = \sum_{i=1}^{3} [\, K_1 \, \mathrm{div}^2 \, \mathbf{e}^i + K_2 \langle \mathbf{e}^i, \mathrm{rot} \mathbf{e}^i \rangle^2 + K_3 \, (\mathbf{e}^i \times \mathrm{rot} \mathbf{e}^i)^2 \,] \tag{37}$$

and $2L$ is the thickness of the nematic layer. The boundary conditions for strong anchoring are

$$\mathbf{e}^i(\pm L) = \mathbf{e}_0^i \, . \tag{38}$$

We will use the approach developed for the orthorhombic nematic LC in [35] for the variational problem with the functional J, the holonomic relationship (5), and boundary conditions (38). This approach makes it possible to identify the nature of the functions that minimize J and satisfy the conditions (5) and (38). This is equivalent to the Ritz variational method. It gives rise to a certain algebraic polynomial with several variables which can be simply analyzed.

The high symmetry of the tetrahedral group leads to the variety of initial unperturbed orientations of nematic bonds with respect to the boundary. Nevertheless, this variety can be shared in the following three different parts by symmetry considerations:

(i) **E** is not parallel to any rotational axis of the nonchiral tetrahedral nematic LC, i.e., **E** is parallel to the primitive rotational axis C_1;

(ii) **E** is parallel to the screw axis $\bar{C}_4$ of the nonchiral tetrahedral nematic LC;

(iii) **E** is parallel to the rotational axis C_3 of the nonchiral tetrahedral nematic LC.

Indeed, let us consider a small deviation of tetrahedral bonds $\mathbf{n}^i$ from their unperturbed positions $\mathbf{n}_0^i$. The deviations of the $\mathbf{e}^i$ triade in the neighborhood of the unperturbed $\mathbf{e}_0^i$ triade according to (4) are also small. Going over to the spherical coordinate system (Fig. 4), introducing the angular coordinates $\tau_i, i = 1, 3$ for vector $\mathbf{e}^1$, $\tau_i, i = 2, 4$ for vector $\mathbf{e}^2$, and using the orthogonality relationship of these vectors we get

$$\langle \mathbf{e}^1, \mathbf{e}^2 \rangle = \sin\tau_1 \sin\tau_2 + \cos\tau_1 \cos\tau_2 \sin(\tau_3 + \tau_4) = 0 \, .$$

We represent the transformations rules of the unperturbed $\mathbf{e}_0^i$ triade as

$$(\, \mathbf{e}^1 \, , \, \mathbf{e}^2 \, , \, \mathbf{e}^3) = (\, \mathbf{e}_0^1 \, , \, \mathbf{e}_0^2 \, , \, \mathbf{e}_0^3) \, \hat{A} \, ,$$

where the three-dimensional operator $\hat{A}(\tau_1, \tau_2, \tau_3)$ is

$$\hat{A} = \begin{pmatrix} \cos\tau_1 \cos\tau_3 & \cos\tau_2 \sin\tau_4 & \cos\tau_1 \sin\tau_2 \sin\tau_3 - \sin\tau_1 \cos\tau_2 \cos\tau_4 \\ \cos\tau_1 \sin\tau_3 & \cos\tau_2 \cos\tau_4 & \sin\tau_1 \cos\tau_2 \sin\tau_4 - \cos\tau_1 \sin\tau_2 \cos\tau_3 \\ \sin\tau_1 & \sin\tau_2 & \cos\tau_1 \cos\tau_2 \cos(\tau_3 + \tau_4) \end{pmatrix} . \tag{39}$$

The angular coordinates $\tau_i(z)$ have the boundary conditions $\tau_i(\pm L) = 0$. Obviously, we have only three independent angular coordinates $\tau_i(z)$ that follow from the orthogonality relation for vectors $\mathbf{e}^1$, $\mathbf{e}^2$. Expanding this relation as a series in τ_i we obtain

$$\tau_3 + \tau_4 + \tau_1\tau_2 \left[1 + \tfrac{1}{3}(\tau_1^2 + \tau_2^2) + \sum_{k=2}^{\infty} P_{2k}(\tau_1, \tau_2) \right] = 0 ,$$

where $P_{2k}(\tau_1, \tau_2)$ is a homogeneous polynomial of the $2k$th degree in τ_1 and τ_2. Let us now symmetrize the expressions for τ_3 and τ_4 by introducing an additional relation $\tau_3 - \tau_4 = 2\tau_5$, then

$$\tau_{3,4} = \pm\tau_5 - \tfrac{1}{2}\tau_1\tau_2 \left[1 + \tfrac{1}{3}(\tau_1^2 + \tau_2^2) + \sum_{k=2}^{\infty} P_{2k}(\tau_1, \tau_2) \right] .$$

In order to find out whether the Fréedericksz transition with zero threshold E^* takes place, it is not necessary to consider the full functional J: according to the Landau theory of phase transition, if the expansion of $F_{T_d} + W$ in the power series in τ_i and $d\tau_i/dz$ includes nonvanishing linear terms τ_i or $d\tau_i/dz$, then the transition occurs in any weak electric field, i.e., the transition threshold is zero (E^*=0). As was shown in [35] for a wide class of functionals, the expansion of F_{T_d} (37) does not include linear terms. These terms originate only from W under certain conditions imposed on $\mathbf{E}$ with respect to the $\mathbf{e}_0^i$ triade. Let us find these conditions. It is easy to show that W can be written in the form

$$W = -\frac{4}{\sqrt{3}} u \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3} E_i^0 E_j^0 E_k^0 \hat{A}_i^1 \hat{A}_j^2 \hat{A}_k^3 , \tag{40}$$

where $E_i^0 = \langle \mathbf{e}_0^i, \mathbf{E} \rangle$. Using the linear part of the orthogonality relationship we will find the linear part W_1 of W with respect to τ_i

$$-\frac{\sqrt{3}}{4u} W_1 = E_2^0[(E_3^0)^2 - (E_1^0)^2]\tau_1 + E_1^0[(E_3^0)^2 - (E_2^0)^2]\tau_2 + E_3^0[(E_2^0)^2 - (E_1^0)^2]\tau_5 . \tag{41}$$

Then we immediately obtain $\mathbf{E}$ directions that preserve the Fréedericksz transition with nonzero threshold E^*:

(ii) $\mathbf{E}$ is parallel to the screw axis $\bar{C}_4$,

$$E_1^0 = E_2^0 = 0 \quad \text{or} \quad E_1^0 = E_3^0 = 0 \quad \text{or} \quad E_2^0 = E_3^0 = 0 ;$$

(iii) $\mathbf{E}$ is parallel to the rotational axis C_3,

$$E_1^0 = E_2^0 = E_3^0 .$$

In any other cases (i) the Fréedericksz transition evolves continuously (E^*=0).

1. $\boldsymbol{E} \parallel \bar{C}_4$

Consider the case where $\mathbf{E} = E\mathbf{e}_0^3$. From (39) and (40) one can obtain up to the fourth power with respect to τ_i

$$2W = \frac{8}{\sqrt{3}} u E^3 \{ \tau_1\tau_2 - \tfrac{2}{3}\tau_1\tau_2 [\tau_1^2 + \tau_2^2] \} . \tag{42}$$

The expression for F_{T_d} up to the fourth power with respect to $d\tau_i/dz$ and τ_i also can be written in the following way:

$$\begin{aligned} 2F_{T_d} = {} & (K_1 + K_3)\left[\left(\frac{d\tau_1}{dz}\right)^2 + \left(\frac{d\tau_2}{dz}\right)^2 \right] + 2K_2 \left(\frac{d\tau_5}{dz}\right)^2 + 2K_3 \frac{d\tau_5}{dz}\left[\tau_1 \frac{d\tau_2}{dz} - \tau_2 \frac{d\tau_1}{dz} \right] \\ & + (2K_1 + 2K_3 - 7K_2)\tau_1\tau_2 \frac{d\tau_1}{dz}\frac{d\tau_2}{dz} + (\tfrac{9}{2}K_2 - K_3)\left[\tau_1^2 \left(\frac{d\tau_2}{dz}\right)^2 + \tau_2^2 \left(\frac{d\tau_1}{dz}\right)^2 \right] \\ & + 2(K_3 - K_2)\left(\frac{d\tau_5}{dz}\right)^2 [\tau_1^2 + \tau_2^2] . \end{aligned} \tag{43}$$

Now we have obtained the well-known density of functional $J_{\bar{C}_4}$ that differs from that one considered for an orthorhombic nematic LC [35] only by the nondiagonalized quadratic terms $\tau_1\tau_2$. By means of canonical transformation and minimizing procedure developed in [35] for similar functionals, like $J_{\bar{C}_4}$, we will obtain after integration of (36) the following expression for the polynomial $J_{\bar{C}_4}(\zeta, \xi, \eta)$:

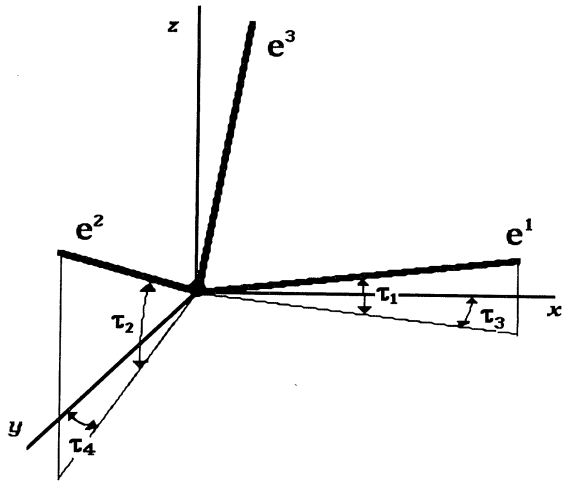

FIG. 4. A perturbed molecular "hedgehog."

$$2J_{\bar{C}_4} = g_1\zeta^2 + g_2\xi^2 + g_3\eta^2 + 2g_4\zeta\xi\eta + g_5\zeta^2\xi^2 + g_6\xi^2\eta^2 + g_7\eta^2\zeta^2 + \tfrac{1}{2}\,(g_8\zeta^4 + g_9\xi^4 + g_{10}\eta^4)\,. \tag{44}$$

In the last expression, ζ and ξ are the amplitudes of the first modes in the cos Fourier expansion for angular deviations $\tau_1 + \tau_2$ and $\tau_1 - \tau_2$ of tetrahedral axis $\bar{C}_4$ from the $\mathbf{E}$ direction correspondingly. η is the similar measure for rotation angle τ_5 around the $\bar{C}_4$ axis. The coefficients g_i can be found in the usual way [35]. We will present the first three of them

$$g_{1,2} = (K_1 + K_3)q^2 \pm \sqrt{3}\varepsilon E^3,\quad g_3 = 2K_2q^2\,, \tag{45}$$

where $q = \pi/2L$ is the wave number, $\varepsilon = 4u/3$ is an electrical "permittivity" of the tetrahedral nematic LC. The other coefficients $g_i(q^2K_j, \varepsilon E^3)$, $i \geq 4$ are continuous functions, also $g_8 > 0, g_q > 0$, $g_{10} > 0$ that follow from the thermodynamical stability condition.

The analysis of $J_{\bar{C}_4}(\zeta, \xi, \eta)$ allows one to find the stationary states separated by the bifurcation points E_m^* where the structural transitions occur. The stationary states are determined by the set of critical points, while the Hessian matrix $((\partial^2 J_{\bar{C}_4}))$ defines the regions of parametric space $\{\zeta, \xi, \eta, E\}$ where the stationary states are stable. The critical points ζ_*, ξ_*, η_* of the polynomial (44) are given by the following system of equations:

$$\partial_\zeta J = \partial_\xi J = \partial_\eta J = 0\,, \tag{46}$$

which has the following solutions that are locally stable in the relevant parts of the parametric space:

(0) *trivial*

$$\zeta_* = \xi_* = \eta_* = 0\,, \tag{47}$$

$$g_1 \geq 0,\ g_2 \geq 0,\ g_3 \geq 0\ :\Rightarrow\ |E| \leq E_1^*\,, \tag{48}$$

(1a) *primary*

$$\zeta_* = \sqrt{-\frac{g_1}{g_8}},\quad \xi_* = \eta_* = 0\,, \tag{49}$$

$$\left.\begin{array}{l} g_1 \leq 0,\ g_8 \geq 0,\ g_2g_8 \geq g_1g_5,\ g_3g_8 \geq g_1g_6, \\ (g_2g_8 - g_1g_5)(g_3g_8 - g_1g_6) + g_1g_8g_4^2 \geq 0 \end{array}\right\}$$

$$\Rightarrow\ E_1^* \leq E \leq E_2^*\,, \tag{50}$$

(1b) *primary*

$$\xi_* = \sqrt{-\frac{g_2}{g_9}},\quad \zeta_* = \eta_* = 0\,, \tag{51}$$

$$\left.\begin{array}{l} g_2 \leq 0,\ g_9 \geq 0,\ g_1g_9 \geq g_2g_5,\ g_3g_9 \geq g_2g_7, \\ (g_1g_9 - g_2g_5)(g_3g_9 - g_2g_7) + g_2g_9g_4^2 \geq 0 \end{array}\right\}$$

$$\Rightarrow\ -E_2^* \leq E \leq -E_1^*\,, \tag{52}$$

(2) *secondary*

$$\zeta_* \neq 0,\ \xi_* \neq 0,\ \eta_* \neq 0\,, \tag{53}$$

$$|E| \geq E_2^*\,, \tag{54}$$

where $\pm E_1^*$ and $\pm E_2^*$ are the primary and secondary bifurcation points accordingly,

$$E_1^* = \sqrt[3]{\frac{K_1 + K_3}{\sqrt{3}\,\varepsilon}}\; q^{\frac{2}{3}}\,. \tag{55}$$

The opposite signs of the fields $+E_m^*$ and $-E_m^*$ mean that they are oppositely directed. The expression for E_2^* cannot be represented in analytic form.

The nonzero solutions are the points of the intersection of three second-order surfaces in the space $\{\zeta^2, \xi^2, \eta^2\}$. The analytic form of such solutions is cumbersome. One can use the symmetry considerations [35] to show that there may be four such solutions. There can also be a situation where there are no solutions at all. The stability of the structures is governed by the positive definiteness of the corresponding Hessian matrix.

This alternation pattern of critical points of the polynomial (44) which are locally stable in different regions of the parametric space is typical for the bifurcation tree in a three-dimensional space with a trivial stem (47) and with primary (49), (51), and secondary (53) bifurcation branches (Fig. 5). At the primary bifurcation points $\pm E_1^*$ the trivial state (47) becomes unstable via a second order structural transition. At the points $\pm E_2^*$ of the secondary bifurcation the primary states (49) and (51) lose their stability via structural transitions of the first or the second order. From the physical standpoint every bifurcation gives rise to a rotation of the tetrahedral "hedgehog" around one of the screw axes $\bar{C}_4$. It might be emphasized that there is a difference between this figure and the one corresponding to the Fréedericksz transition in the orthorhombic nematic LC [35]. Of course, this

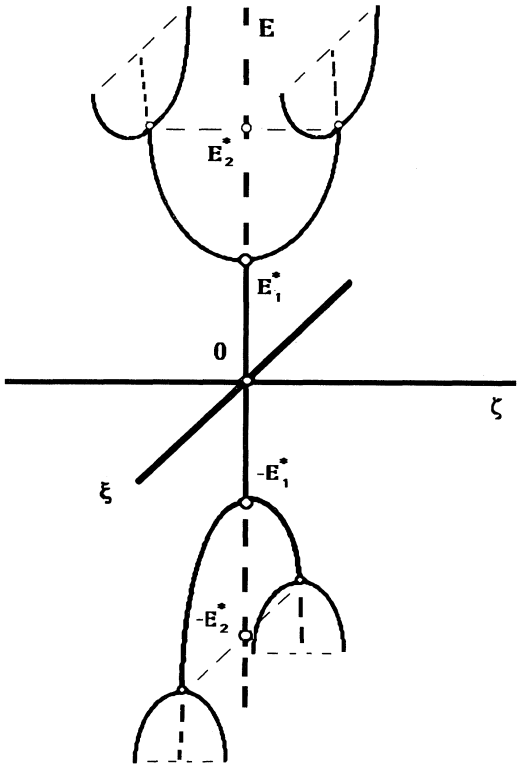

FIG. 5. Bifurcation tree of the Fréedericksz transition in tetrahedral nematic ($\mathbf{E} \parallel \bar{C}_4$): $\pm E_1^*$ and $\pm E_2^*$ are the primary and the secondary bifurcation points, respectively.

difference is concerned with the unparity property (2) of the order parameter U_{ijk}. In this case, the Fréedericksz transition in the tetrahedral nematic LC occurs if $\mathbf{E}$ is both *parallel* and *antiparallel* to the $\bar{C}_4$ axis that also distinguishes the tetrahedral phase from orthorhombic and cubic [36] phases.

2. $E \parallel C_3$

We have here $\mathbf{E} = (\mathbf{e}^1 + \mathbf{e}^2 + \mathbf{e}^3)E/\sqrt{3}$ and this case can be analyzed in the same way as the preceding one. Not going into analytical details, let us consider the corresponding polynomial of free energy $J_{C_3}(\zeta, \xi, \eta)$ [let us note that the expressions for polynomials (44) and (56) can be obtained in a more simple way by use of the integrity basis of invariant polynomial for the point symmetry groups C_{2v} and C_{3v}]

$$2J_{C_3} = f_1(\zeta^2 + \xi^2) + f_2\eta^2 + f_3\zeta(\zeta^2 - 3\,\xi^2) + f_4\eta^4 + f_5\eta^2(\zeta^2 + \xi^2) + f_6(\zeta^2 + \xi^2)^2 \,. \tag{56}$$

Here ζ and ξ are the amplitudes of the first modes in the cos Fourier expansion for angular deviations of the tetrahedral axis C_3 from the $\mathbf{E}$ direction, η is a similar angular measure for the rotation of tetrahedral bonds around the C_3 axis. The first two coefficients f_i are

$$f_1 = \tfrac{1}{3}(3K_1 + K_2 + 2K_3)q^2 - \tfrac{5}{3}\,\varepsilon E^3,$$
$$f_2 = \tfrac{2}{3}\,(2K_2 + K_3)q^2 \,. \tag{57}$$

The other coefficients $f_i(q^2K_j, \varepsilon E^3)$, $i \geq 3$ are continuous functions, also $f_4 > 0$, $f_6 > 0$ which follows from the thermodynamical stability condition. This kind of potential is also well known [37]. It can be easily shown that (56) gives one primary bifurcation point E_1^*

$$E_1^* = \sqrt[3]{\frac{3K_1 + K_2 + 2K_3}{5\varepsilon}}\; q^{\frac{2}{3}} \tag{58}$$

and one secondary bifurcation point E_2^*.

Since Eq. (56) contains cubic terms, the structural transition in point E_1^* is of the first order that implies the presence of hysteresis. It is more convenient to analyze the critical points of the polynomial (56) in polar coordinates ρ and ψ which are defined by the relations $\zeta = \rho\cos\psi$, $\xi = \rho\sin\psi$. The sequence of the stable states is as follows:

(0) *trivial*

$$\rho_* = \eta_* = 0\,, \psi_* \text{ is arbitrary} \,, \tag{59}$$

$$f_1 \geq 0, \;\; f_2 \geq 0 \;\; : \Rightarrow \;\; E \leq E_1^* \,, \tag{60}$$

(1) *primary*

$$\rho_* = \frac{3}{8}\frac{|f_3|}{f_6} \pm \sqrt{\frac{9}{64}\left(\frac{f_3}{f_6}\right)^2 - \frac{1}{2}\frac{f_1}{f_6}},$$
$$\eta_* = 0, \;\; \psi_* = m\frac{\pi}{3}, \; m \geq 1 \,, \tag{61}$$

$$f_1 \leq 0 \text{ is stable}, \;\; 0 \leq f_1 \leq \frac{9}{32}\,\frac{f_3^2}{f_6} \text{ is metastable} \,,$$
$$E_1^* \leq E \leq E_2^* \,, \tag{62}$$

(2) *secondary*

$$\rho_* = \frac{3|f_3|f_4 \pm \sqrt{9f_3^2f_4^2 - 4\Delta_1\Delta_2}}{2\Delta_1},$$
$$\eta_*^2 = \frac{\Delta_2 - 3|f_3|\rho_*}{2f_4\Delta_1}, \;\; \psi_* = m\frac{\pi}{3}, \; m \geq 1 \tag{63}$$

$$\Delta_1 = 4f_4f_6 - f_5^2 \neq 0, \;\; \Delta_2 = f_1f_4 - f_2f_5 \,,$$
$$E \geq E_2^* \,. \tag{64}$$

The expression for E_2^* is defined by the real solution of the equation $\Delta_2 = 3|f_3|\rho_*$. There are some more degenerated cases ($\Delta_1 = 0$) which can lead to the change of the transition order in the secondary bifurcation point or even to its vanishing. The details of the whole procedure will not be discussed here. Unlike the preceding case ($\mathbf{E} \parallel \bar{C}_4$), the Fréedericksz transition occurs now only when $\mathbf{E}$ has the *same* direction as the C_3 axis (Fig. 6).

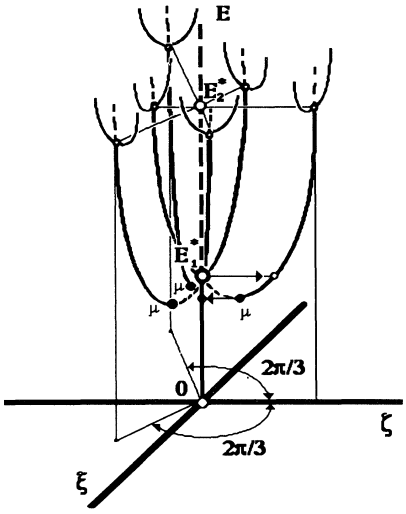

FIG. 6. Bifurcation tree of the Fréedericksz transition in tetrahedral nematic ($\mathbf{E} \parallel C_3$): E_1^* and E_2^* are the primary and the secondary bifurcation points. A hysteresis is shown in the vicinity of E_1^*.

E. Behavior of the chiral tetrahedral phase in an external field

Consider the chiral tetrahedral T phase in electric field $\mathbf{E}$. Now we have another scenario: the inhomogeneous spatial distribution of tetrahedral bonds (Fig. 2) makes the distortion of unperturbed T phase valid at any weak field $\mathbf{E}$. But there arises another question — does the field untwist the helices of chiral tetrahedral bonds as well as it does with the uniaxial helix in the case of the cholesteric LC ($G = D_\infty$)?

In order to give an answer to this question let us consider the behavior of the unbounded T_d phase in an electric field. It is easy to show that all tetrahedral bonds will be oriented homogeneously in such a way that the rotational axis C_3 of the nonchiral tetrahedral phase will coincide with the $\mathbf{E}$ direction. Naturally, the possible direction of the C_3 axis — along the field or the opposite direction — depends on the sign of u. Returning to the chiral tetrahedral nematic LC in an electric field, it is now clear that we have two mechanisms of the field influence on the uniaxial helices of the T phase: untwisting of helices and reorientation of their axes in the space.

1. Untwisting of the C_2 helix

The expression for the free energy J_2 contains a twist angle ϕ of the tetrahedral bonds around the helical axis C_2 in a plane perpendicular to this axis and a deviation angle χ between the helical axis and the $\mathbf{E}$ field

$$J_2 = \frac{K_2}{L}\int_0^L \left[\left(\frac{d\phi}{dz} - \mu_{C_2}^*\right)^2 - (\mu_{C_2}^*)^2 - \tfrac{1}{2}\,\sigma_2^{-2}\cos\chi\,\sin^2\chi\,\sin 2\phi \right] dz\,. \tag{65}$$

Here the helical axis is directed along the z axis, $\mu_{C_2}^*$ is determined in (18), an electric coherence length σ_2 is given by

$$\sigma_2^2 = \frac{1}{2\sqrt{3}}\,\frac{K_2}{\varepsilon E^3}\,. \tag{66}$$

An equilibrium state that minimizes J_2 is obtained from a solution of the Euler- Lagrange equations derived from (65) with respect to ϕ and χ,

$$\frac{d^2\phi}{dz^2} + \tfrac{1}{2}\,\sigma_2^{-2}\cos\chi\,\sin^2\chi\,\cos 2\phi = 0\,, \tag{67}$$

$$\sin\chi\,(3\cos^2\chi - 1) = 0\,. \tag{68}$$

The last equation gives the deviation angle χ_2^* which minimizes the free energy and does not depend on the twist angle ϕ. One can show that the minimum of J_2 corresponds to $\chi_2^* = \arctan(\pm\sqrt{2})$, where "+" or "−" signs are determined by the sign of ε.

Equation (67) is a time-independent sine *Gordon* equation. Inserting the value of χ_2^* into (67) we will obtain a periodic solution

$$\phi(z,\mathbf{k}) = -\frac{\pi}{4} + \arcsin\left[\,\mathrm{sn}\left(\frac{z}{\mathbf{k}\sigma_2}\sqrt[4]{\frac{4}{27}}\right)\right] \tag{69}$$

with the pitch h_2 of the perturbed helical structure

$$h_2 = 2\sqrt[4]{108}\,\sigma_2\,\mathbf{k}\,\mathbf{K}(\mathbf{k})\,. \tag{70}$$

Here $\mathrm{sn}(z,\mathbf{k})$ is the Jacobi elliptic function, $\mathbf{K}(\mathbf{k})$ denotes the complete elliptic integral of the first kind of modulus $\mathbf{k}$, where the constant $\mathbf{k}$ is determined from the following equation with the complete elliptic integral of the second kind $\mathbf{E}(\mathbf{k})$ as:

$$\mathbf{E}(\mathbf{k}) = \frac{\pi}{2}\,\mu_{C_2}^*\,\mathbf{k}\,\sigma_2\sqrt[4]{\frac{27}{4}}\,. \tag{71}$$

Using the two last equations one can show that the helical pitch h_2 increases with an increase of E and diverges as $h_2(E) \propto -h_2^0\,\ln(E_{th} - E)$ in the vicinity of threshold field E_{th} which is given by

$$E_{th} = \left(\frac{\pi\sqrt{3}}{4}\kappa\right)^{\frac{2}{3}}\sqrt[3]{\frac{K_2}{\varepsilon}}\,. \tag{72}$$

Thus, the chiral-nonchiral tetrahedral nematic phase transition is shown to occur continuously at $E = E_{th}$. The free energy J_2^* is given by expression

$$J_2^* = \frac{2}{\sqrt{27}}\,\frac{K_2}{\sigma_2^2}\left(\frac{1}{2} - \frac{1}{\mathbf{k}^2}\right) = \begin{cases} -K_2\kappa^2\,, & E \to 0 \\ -(\frac{\pi}{2})^2\,K_2\kappa^2\,, & E \to E_{th}\,. \end{cases}$$

This obviously confirms the energetic preference of helix untwisting.

2. Deviation of the C_3 helix

In contrast to the case considered above the behavior of C_3 helices in an external field does not lead to the untwisting of the helical structure at all. Indeed, let us write a free energy J_3 of this chiral LC choosing for convenience an appropriate orthonormalized coordinate system that is based on the three unitary vectors $\mathbf{N}^i$

$$\mathbf{N}^1 = \mathbf{n}^1 , \quad \mathbf{N}^2 = \frac{1}{2\sqrt{2}} (3\mathbf{n}^2 + \mathbf{n}^1) ,$$

$$\mathbf{N}^3 = \frac{1}{2} \sqrt{\frac{3}{2}} (2\mathbf{n}^3 + \mathbf{n}^2 + \mathbf{n}^1) . \tag{73}$$

Using the notations for the twist angle ϕ of the tetrahedral bonds around helical axis C_2 and a deviation angle χ between the helical axis the and $\mathbf{E}$ field, we will obtain the expression for J_3

$$J_3 = \frac{K_2}{L} \int_0^L \left[\left(\frac{d\phi}{dz} - \mu^*_{C_3} \right)^2 - \kappa \mu^*_{C_3} + \tfrac{1}{2} \sigma_3^{-2} \sin^3 \chi \sin 3\phi + \Phi(\chi) \right] dz , \tag{74}$$

$$\Phi(\chi) = \frac{4\sqrt{2}}{3} \sigma_3^{-2} (3\cos\chi - 5\cos^3\chi) .$$

The helical axis coincides with the z axis, $\mu^*_{C_3}$ is determined in (17), and the electric coherence length σ_3 is given by

$$\sigma_3^2 = 3\sqrt{2} \frac{K_2}{\varepsilon E^3} . \tag{75}$$

The Euler-Lagrange equations for functional (74) read

$$\frac{d^2\phi}{dz^2} - \frac{3}{4} \sigma_3^{-2} \sin^3\chi \cos 3\phi = 0 , \tag{76}$$

$$\sin\chi \left(5\sqrt{2} \cos^2\chi + \tfrac{3}{16} \sin 2\chi \sin 3\phi - \sqrt{2} \right) = 0 . \tag{77}$$

The last equation has only one solution, $\sin\chi_3^* = 0$, which does not depend on the twist angle ϕ: $\chi_3^* = 0$ corresponds to $\varepsilon > 0$ and $\chi_3^* = \pi$ corresponds to $\varepsilon < 0$. It means that the helical axis deviates in such a way that $\mathbf{E}$ is directed along it. As follows from (76), the C_3 helical structure does not untwist. The free energy J_3^* is

$$J_3^* = -K_2 \kappa \mu^*_{C_3} - \tfrac{8}{9} \varepsilon E^3 ,$$

i.e., the elastic energy of unperturbed C_3 helices and the electrostatic energy of the nonchiral tetrahedral nematic phase in the $\mathbf{E}$ field contribute to J_3^* additively.

3. Chiral tetrahedral phase in crossed fields

As we have seen in the preceding sections, there is a continuous degeneracy of C_2 helical axes at the conic surface around the direction of the external field. We can remove this degeneracy in the chiral T phase applying two crossed external fields of different nature — electric $\mathbf{E}$ and magnetic $\mathbf{H}$ fields. One can expect as well that the crossed external fields will give rise to the deviations of the C_3 helical structure. The calculation is similar to the previous one, and we will give a brief list of derived expressions and short comments on them.

C_2 helix. Consider the C_2 helical structure put in crossed $\mathbf{E}$ and $\mathbf{H}$ fields, $\langle \mathbf{E}, \mathbf{H} \rangle = EH\cos\varsigma$. The free energy $J_{2\otimes}$ of this system is

$$J_{2\otimes} = \frac{K_2}{L} \int_0^L \left[\left(\frac{d\phi}{dz} - \mu^*_{C_2} \right)^2 - (\mu^*_{C_2})^2 - \tfrac{1}{2} G_1 \sin 2\phi - \tfrac{1}{2} G_2 \cos 2\phi \right] dz , \tag{78}$$

$$G_1 = \sigma_{2E}^{-2} \cos\chi_E \sin^2\chi_E + \sigma_{2H}^{-2} \cos\chi_H \sin^2\chi_H \cos 2\varrho ,$$

$$G_2 = \sigma_{2H}^{-2} \cos\chi_H \sin^2\chi_H \sin 2\varrho .$$

As before, the helical axis here coincides with the z axis; χ_E and χ_H are the deviation angles between this axis and the directions of $\mathbf{E}$ and $\mathbf{H}$, respectively, ϱ is a projection of the angle ς on the plane perpendicular to the helical axis. There exists a relation

$$\cos\varsigma = \cos\chi_E \cos\chi_H + \sin\chi_E \sin\chi_H \cos\varrho , \tag{79}$$

where σ_{2E} is given by (66) and σ_{2H} is defined as $\sigma_{2H}^2 = \sigma_{2E}^2 (E/H)^3$. (Strictly speaking, it would be worthwhile introducing two separate interaction constants of the tetrahedral phase with electric and magnetic fields: instead of ε, we would have two permittivities, ε_E and ε_H, for each field. It would lead to the renormalization of σ_{2E}, σ_{2H} and would not change the following considerations.) The Euler-Lagrange equations that describe an equilibrium state of this system read

$$\frac{d^2\phi}{dz^2} + \tfrac{1}{2} G_1 \cos 2\phi - \tfrac{1}{2} G_2 \sin 2\phi = 0 , \tag{80}$$

$$\partial_{\chi_E} (G_1^2 + G_2^2) = \partial_{\chi_H} (G_1^2 + G_2^2) = 0 . \tag{81}$$

Two equations (81) give the deviation angles χ^*_{2E}, χ^*_{2H} which minimize the free energy $J_{2\otimes}$ and do not depend on the twist angle ϕ. Inserting the expressions for G_1, G_2, ϱ in (81) and omitting the simple algebraic calculations we obtain

$$\sigma_{2E}^{-2} \cos\chi_E (3\cos^2\chi_E - 1) + \sigma_{2H}^{-2} \cos\chi_H (3\cos^2\chi_H - 1) = 0 , \tag{82}$$

$$\cos^2\chi_E - 2\cos\varsigma \cos\chi_E \cos\chi_H + \cos^2\chi_H = \tfrac{1}{2} \sin^2\varsigma . \tag{83}$$

These equations generalize Eq. (68) in the case of non-collinear fields and they are reduced to it by setting $\varsigma = 0$. In the $(\cos\chi_E, \cos\chi_H)$ plane, Eqs. (82) and (83) describe two algebraic curves of the third and second order, respectively, which at least have one pair of intersection points. [In the polar coordinate system, curve (82) passes through the origin of coordinates and has two opposite asymptotic directions where it goes to infinity. Curve (83) is a simple ellipse.] Moreover, under certain conditions for the values of E, H, ς the curves will have two or three pairs of intersection points. This means that we could deal with the first order transition between C_2 helical structures during their evolution caused by the applied **E** and **H** fields. Thus we have at least one real solution χ^*_{2E}, χ^*_{2H} which depends on the values E, H of applied fields. The orientation of the C_2 helical axis deviates with the increase of E and H.

Simultaneously, this helical structure will untwist according to the time-independent sine *Gordon* equation (80). A periodic solution of it can be obtained in terms of the Jacobi elliptic function. The pitch $h_{2\otimes}$ of the perturbed helical structure is

$$h_{2\otimes} = 4\,(G^2_{1*} + G^2_{2*})^{-\frac{1}{4}}\,\mathbf{k}\,\mathbf{K}(\mathbf{k})\,, \tag{84}$$

where $G_{i*} = G_i\ (\chi^*_{2E}, \chi^*_{2H})$. The following expression gives the values of threshold fields E_{th}, H_{th} in the implicit form:

$$G^2_{1*} + G^2_{2*} = \left(\frac{\pi}{2}\,\kappa\right)^4\,,$$

where the C_2 helix is fully untwisted. In the (E_{th}, H_{th}) plane, the last equation describes a continuous algebraic curve.

C_3 helix. Consider the C_3 helical structure in the crossed **E** and **H** fields which are not collinear. A free energy $J_{3\otimes}$ of this system is

$$J_{3\otimes} = \frac{K_2}{L}\int_0^L \left[\left(\frac{d\phi}{dz} - \mu^*_{C_3}\right)^2 - \kappa\,\mu^*_{C_3} + \tfrac{1}{2}\,(G_3\sin 3\phi + G_4\cos 3\phi) + \Phi(\chi_E) + \Phi(\chi_H)\right] dz, \tag{85}$$

$$G_3 = \sigma^{-2}_{3E}\,\sin^3\chi_E + \sigma^{-2}_{3H}\,\sin^3\chi_H\,\cos 3\varrho\,,$$

$$G_4 = \sigma^{-2}_{3H}\,\sin^3\chi_H\,\sin 3\varrho\,,$$

where σ_{3E} is given by (75), $\sigma^2_{3H} = \sigma^2_{3E}(E/H)^3$, and the function $\Phi(\chi)$ is defined in (74). The Euler-Lagrange equations read

$$4\sqrt{G^2_3 + G^2_4}\,\partial_{\chi_E}\Phi(\chi_E) + \sin 3\phi\,\partial_{\chi_E}(G^2_3 + G^2_4) = 0\,, \tag{86}$$

$$4\sqrt{G^2_3 + G^2_4}\,\partial_{\chi_H}\Phi(\chi_H) + \sin 3\phi\,\partial_{\chi_H}(G^2_3 + G^2_4) = 0\,.$$

They have only one trivial solution G_{3*}, G_{4*}, which does not depend on ϕ

$$G_{3*} = G_{4*} = 0\,. \tag{87}$$

These equations generalize Eq. (77) for the case of crossed fields. In the crossed fields, the C_3 helical structure will not untwist. However, the deviation of the helical axis depends now on the magnitudes of the fields E and H. Equations (87) determine the equilibrium direction χ^*_{3E}, χ^*_{3H} of the C_3 helical axis as a function of the independent variables E, H, $\cos\varsigma$. If the directions of the external fields do not coincide with the helical axis, there are four different orientations determined by an algebraic system corresponding to four different values of $\varrho = 0,\ \frac{\pi}{3},\ \frac{2\pi}{3},\ \pi$

$$\cos\chi_E\,\cos\chi_H + \sin\chi_E\,\sin\chi_H\,\cos\varrho = \cos\varsigma\,, \tag{88}$$

$$\sigma^{-2}_{3E}\,\sin^3\chi_E + \sigma^{-2}_{3H}\,\sin^3\chi_H\,\cos 3\varrho = 0\,.$$

The competition between these four solutions leads to the selection of the equilibrium state, corresponding to the minimum of the sum $\Phi(\chi_E) + \Phi(\chi_H)$. The first order transitions between different helical orientations are expected with the variation of the applied fields.

F. Defects in the tetrahedral nematic LC

The current topological $d_\ominus$-dimensional defect classification [38] labels singularities in three-dimensional space by the conjugacy classes of the absolute homotopy groups $\pi_{d_\oplus}(\mathcal{V})$, where $d_\oplus = 2 - d_\ominus$. The degeneracy space $\mathcal{V}$ of the order parameter Q is defined as a coset space $\mathcal{G}/\mathcal{P}$, $\mathcal{G}$ is the unbroken symmetry group and $\mathcal{P}$ is the subgroup of (preserved) symmetry of the phase. The defect that corresponds to the trivial conjugacy class $\{1\}$ can be smoothed out by a local order-parameter fluctuation and, therefore, is denoted as topologically unstable.

Using general properties of the symmetry groups [SO(3) is a connected component of O(3), T is a connected component of T_d and does not contain continuous rotation around an axis] it is easy to show the absence of the stable point defects ($d_\ominus = 0$) and the surface defects ($d_\ominus = 2$) in chiral and nonchiral tetrahedral nematic LC's

$$\pi_0(\mathrm{O}(3)/T_d) = \pi_0(\mathrm{SO}(3)/T) = \{1\}\,,$$

$$\pi_2(\mathrm{O}(3)/T_d) = \pi_2(\mathrm{SO}(3)/T) = \{1\}\,. \tag{89}$$

Line defects ($d_\ominus = 1$) were studied in [16] where another mechanism of the topological instability of these defects was pointed out in addition to the above-mentioned *relaxation* process : one defect can be transformed into the other via *catalyzation* by the third defect line. This classification used for tetrahedral phase leads [16] to stable disclinations which are directed along a threefold rotational axis of tetrahedral phase. This fact is reflected

in the existence of a nontrivial fundamental group

$$\pi_1(\mathrm{O}(3)/T_d) = \pi_1(\mathrm{SO}(3)/T) = \tilde{T} , \qquad (90)$$

where $\tilde{T}$ is a binary group of T with seven conjugacy classes assembled into three subsets

$$\{C_0, \bar{C}_0, C_4^2\} \ , \ \{C_3, \bar{C}_3\} \ , \ \{C_3^2, \bar{C}_3^2\} .$$

Let us build the distribution of nonchiral tetrahedral bonds around the disclination line L of the above mentioned type [Figs. 7(a)–(c)] by means of the Volterra process for the partially ordered fluids [39]. On this line, parallell to the threefold rotational axis C_{3v}, the directions of the tetrahedral bonds are undefined. However, we will try to consider this core of defect by the approach developed in [40] for the disclination core in a uniaxial nematic LC. Consider expression (3) for the free energy F of T_d nematic LC. According to the definition of the order parameter U_{ijk}

$$\mathrm{Tr}\, Q_3^2 = \sum_{i,j,k} U_{ijk}U_{ijk} = \tfrac{32}{9}u^2 . \qquad (91)$$

The free energy (3) is a function only of Tr Q_3^2 and the symmetry of the order parameter is higher than in the tetrahedral case. The only constraint comes from the last equation where u can be found by the minimization of the free energy F. As has been mentioned in Sec. III C, one can use a model of seven-componential spins of the fixed length instead of the third rank traceless tensor U_{ijk} (Appendix). The last equation manifests this property and determines the degeneracy space $\mathcal{V}$ as a six-dimensional sphere S^6 in the seven-dimensional space of the components of matrix U_{ijk}. This fact immediately leads to topological removability of the singularities in the core of disclination, since $\pi_d(S^6) = \{1\}$ for $d = 0, 1, 2$. As can be seen in Fig. 7(d), this removability occurs due to the appearance of a uniaxial phase with sixfold rotational axis C_{6v} in the center of the core.

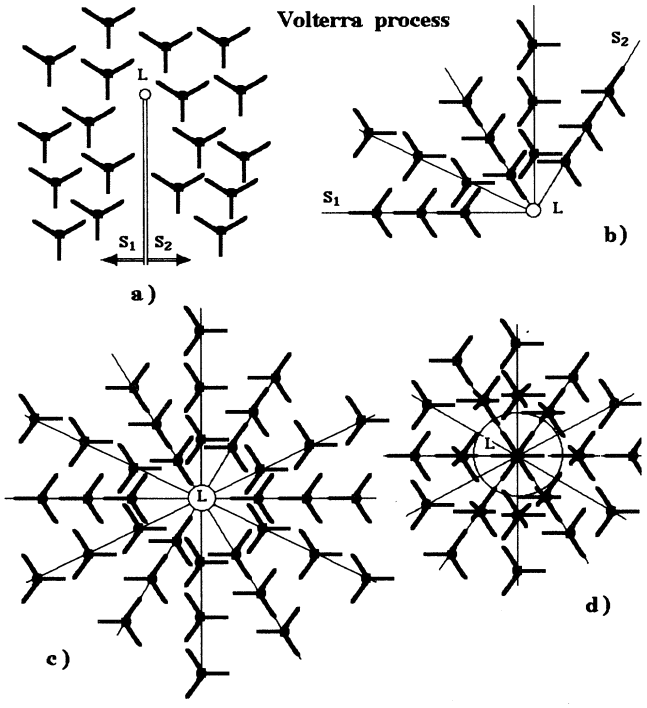

FIG. 7. The origin of the disclination line in the tetrahedral nematic via the Volterra process. Disclination line L is along the threefold rotational axis C_{3v} (normal to the plane of the page): (a) the cross section of the tetrahedral nematic LC by the plane $L - S_1S_2$; (b) the displacement of the lips $L - S_1$ and $L - S_2$ of the cutting surface with respect to each other; (c) the disclination line L after viscous relaxation of the structure; (d) disclination core.

IV. CONCLUSION

The present paper is devoted to the nematic liquid crystals with tetrahedral point symmetry groups (G) — chiral ($G = T$) and nonchiral ($G = T_d$) tetrahedral nematic LC's which were not previously discussed. Nevertheless, they occupy a natural place among other nonuniaxial nematic LC's — biaxial, cubic, icosahedral. From all nematic phases, the tetrahedral phase is the only one that has an order parameter Q_3 of the odd rank. It leads to some peculiarities of physical properties of this phase.

The phase transition from isotropic liquid into tetrahedral nematic LC is of the second order via a supercritical bifurcation, or of the first order via a subcritical bifurcation. This behavior distinguishes tetrahedral LC from other nematic LC's with tensor order parameter of even rank, where the phase transition from isotropic liquid is of the first order via a transcritical bifurcation. In the framework of the Maier-Saupe approach, it has been shown that the transition from isotropic liquid into nonchiral tetrahedral nematic $G = T_d$ is always of the second order, and the temperature T^* of this transition has been found.

It is shown that the continuous equilibrium state of chiral tetrahedral nematic LC's manifests itself as a helical structure of two possible kinds — uniaxial phases with helical axes along the rotational axes C_2 or C_3. The behavior of the helical structures in the external $\mathbf{E}$ field is determined due to the reorientation of the helical axes with respect to the field direction for both kinds of spirals. Besides, the applied field untwists only the C_2 spiral structure, and its pitch h_2 increases with the increase of E and diverges logarithmically in the vicinity of the untwisting threshold field E_{th}.

In the framework of the mean-field approximation, the polarizability p_3 of the tetrahedral nematic LC in the electric field behaves as $p_3 \propto E^4$.

Among other problems concerned with nonuniaxial nematics, a traditional one is the Fréedericksz transition in the nonchiral tetrahedral phase. The high symmetry of tetrahedral group T_d and a strong anchoring of nematic bonds at the boundaries of the infinite plane-parallel slab choose only two directions of $\mathbf{E}$ which pre-

serve the Fréedericksz transition with nonzero threshold E^*. Namely, the Fréedericksz transition is possible when **E** is parallel to the screw axis $\bar{C}_4$, or to the rotational axis C_3 of the unperturbed tetrahedral phase. In both cases the bifurcation trees have been found, and the threshold fields at the first and second bifurcation points are obtained.

A disclination core in the nonchiral tetrahedral nematic is analyzed: it is free of singularities due to the appearance of a uniaxial phase with sixfold rotational axis C_{6v} in the center of the core. The point and surface defects are unstable in the tetrahedral nematic LC.

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APPENDIX

Let us show that Tr Q_3^2 can be represented as a sum of seven squares of independent components U_{ijk}. According to the definition of the unitary *septor*

$$U_{111}+U_{112}+U_{113}=U_{221}+U_{222}+U_{223} = U_{331}+U_{332}+U_{333}=0\,. \quad \text{(A1)}$$

Then,

$$\begin{aligned}\mathrm{Tr}\, Q_3^2 = \sum_{i,j,k} U_{ijk}U_{ijk} &= 6\,U_{123}^2+2\,(U_{112}U_{113} \\ &\quad +U_{221}U_{223}+U_{331}U_{332}) \\ &\quad +4\,(U_{112}^2+U_{113}^2+U_{221}^2 \\ &\quad +U_{223}^2+U_{331}^2+U_{332}^2)\,. \quad \text{(A2)}\end{aligned}$$

This quadratic form is positively defined and can be diagonalized in the canonical basis Υ_i

$$\begin{aligned}U_{123}=\frac{1}{\sqrt{6}}\Upsilon_1\,,\quad \begin{pmatrix}U_{112}\\U_{113}\end{pmatrix}&=\hat{\Lambda}\begin{pmatrix}\Upsilon_2\\\Upsilon_3\end{pmatrix}\,,\\ \begin{pmatrix}U_{221}\\U_{223}\end{pmatrix}&=\hat{\Lambda}\begin{pmatrix}\Upsilon_4\\\Upsilon_5\end{pmatrix}\,,\\ \begin{pmatrix}U_{331}\\U_{332}\end{pmatrix}&=\hat{\Lambda}\begin{pmatrix}\Upsilon_6\\\Upsilon_7\end{pmatrix}\,,\end{aligned}$$

where the transformation operator $\hat{\Lambda}$ is

$$\hat{\Lambda}=\begin{pmatrix}\frac{1}{\sqrt{10}} & -\frac{1}{\sqrt{6}}\\ \frac{1}{\sqrt{10}} & \frac{1}{\sqrt{6}}\end{pmatrix}\,.$$

Then, one obtains from (91) the equation of a six-dimensional sphere S^6

$$\mathrm{Tr}\, Q_3^2=\sum_{i=1}^{7}\Upsilon_i^2=\frac{32}{9}\,u^2\,. \quad \text{(A3)}$$

Thus, one can use a model of seven-component spins $\boldsymbol{\Upsilon}$ of fixed length instead of the third rank traceless tensor U_{ijk}.

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