Phenomenological approach to the problem of the K_{13} surfacelike elastic term in the free energy of a nematic liquid crystal

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We consider the mathematical foundations of continuum theories of nematic liquid crystals of the Frank-Oseen form which include, in addition, the surfacelike K_{13} term. Such theories present problems because (i) the free-energy functional F_2, quadratic in the director derivatives, is unbounded from below and hence possesses no minima unless K_{13} is strictly zero; and (ii) microscopic theories indicate that in the general case K_{13} does not vanish. The continuum theory presupposes the existence of weak director deformations. This is not consistent with the idea, proposed by Oldano and Barbero, that there should be strong subsurface director deformations, which are shown in the present paper to be a formal consequence of (i). Instead we propose a resolution of the K_{13} problem which is consistent with weak director distortions alone. The resolution involves a formal consideration of all the terms in the total free energy containing high-order derivatives, the infinite sum of which, R_∞, bounds the total free energy F_2+R_∞ from below. A consequence of this resolution is that the Euler-Lagrange equations which follow from a naive consideration of the Oseen-Frank free-energy functional F_2, and which appear to give rise to a nonminimal family thereof, in fact give rise to a minimal family of director distributions of the total free energy F_2+R_∞. Moreover, no specific information on higher-order elastic terms enters the theory. The theory further allows consideration of the derivative-dependent terms in the anchoring energy. Each such derivative is shown to be proportional to a small parameter. As a result, all derivative-dependent anchoring terms are much smaller than the usual Rapini-Popoular term.

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I. INTRODUCTION

Macroscopic structures in nematics are described by a director distribution $\mathbf{n}(\mathbf{r})$. This can be found by minimizing a free-energy functional (henceforth FE in this paper). The important part of this functional from our point of view will be that part which is quadratic with respect to the sign ∂ of the director derivatives; we shall label it F_2. F_2 contains distinct contributions. One contribution is the standard Frank contribution f_F. In addition there are two divergence terms. This can be expressed as [1]

$$F_2=\int dV\{f_F+K_{13}\nabla\cdot[\mathbf{n}(\nabla\mathbf{n})] -(K_{22}+K_{24})\nabla\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})+\mathbf{n}\times\nabla\times\mathbf{n}]\} =\int dV\, f_F+\int dS(f_{13}+f_{24}) , \quad (1)$$

where

$$f_F=\tfrac{1}{2}[K_{11}(\nabla\cdot\mathbf{n})^2+K_{22}[\mathbf{n}\cdot(\nabla\times\mathbf{n})]^2+K_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2] , \quad (2)$$

$$f_{13}=K_{13}(\boldsymbol{\nu}\cdot\mathbf{n})(\nabla\cdot\mathbf{n}) , \quad (3)$$

$$f_{24}=-(K_{22}+K_{24})\boldsymbol{\nu}\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})+\mathbf{n}\times\nabla\times\mathbf{n}] . \quad (4)$$

In formula (1), the bulk integral over the terms which are of divergence form is transformed by means of Gauss's theorem into the integral over the nematic surface S, whose external normal is $\boldsymbol{\nu}$, with $|\boldsymbol{\nu}|=1$.

Most traditional treatments of the physics of nematic phases have only considered f_F; the divergence terms in the FE have essentially been ignored. More recently, however, there has been renewed interest in the physical content that these terms might convey. One argument which has been put forward to justify ignoring the divergence terms is that divergence terms do not change the Euler-Lagrange equations, and that therefore they may be omitted. In our opinion this argument is not satisfactory, and a large number of papers on this problem have appeared in the literature which show that this point of view is untenable (a detailed analysis of the reasons why the surfacelike terms have been ignored is given in Ref. [2]). Indeed, it turns out that basic mathematical difficulties appear, associated with the minimization of the total functional F_2. The problem derives from the fact that the standard variational analysis deals with functionals whose surface contribution contains no derivative-dependent terms, whereas the surface part of the functional F_2 depends on the director derivative ∂n. Such terms appear in the surface integral in F_2 in the two divergence terms, which we shall refer to as the K_{13} and K_{24} terms. An extremal family of functions for the standard functional is known to satisfy the Euler-Lagrange equations. However a minimizing procedure for the functional F_2 is not known. Moreover, specific physical effects associated with the K_{13} and K_{24} terms have not been derived.

The present situation is that the problem of the K_{24}

term has been solved: a minimization procedure for the FE with the K_{24} term has been proposed [3,4]; physical effects whose very occurrence critically depend on the value of K_{24} have been shown to exist [2,4–6], and even estimates of the value of K_{24} have been made [6,7].

In the case of the K_{13} term, by contrast, minimization procedures are now under discussion [8–15] and, as a consequence, the corresponding physical effects cannot be predicted unambiguously.

A formal treatment of the K_{13} term in the FE results in the idea of strong (formally, infinite) spontaneous subsurface director deformations. Barbero and Oldano [8,10] were the first to point out these unexpected, indeed paradoxical consequences of the presence of the K_{13} term in the nematic FE. Further discussion of these consequences [10,13] has in fact revealed the inconsistency of such infinite subsurface deformations. The next important step in comprehending the problem has been made by Barbero, Madhusudana, and Oldano [11]. These authors, having understood the need to deal with finite deformations, explicitly introduced in the theory certain terms of the fourth order in the derivative sign ∂, and so additional fourth-order elastic constants. Though this restricts the deformations, they are still sufficiently strong that the relevant length scale is of molecular dimensions [11,13,16,17]. Since the weakness of the deformations is crucial for the very derivation of the FE expression (1), it is evident that an approach leading to such strong deformations in the nematic liquid crystal is inadequate.

In order to show how the consequences of this approach are far different than the standard ideas about the nematic phase, we consider the following example. If follows from [11] that the director tilt θ on the nematic surface S undergoes a change $\Delta\theta\sim 1$ in a distance of the order of the molecular length L_M corresponding to the surface energy density $f_{13}\sim -|K_{13}(\Delta\theta/L_M)| \sim -|K_{13}/L_M|$. At the same time the characteristic scale L of the standard nematic deformations is much greater than L_M; the energy f_0 contained in the subsurface layer of thickness L_M can be estimated as $f_0\sim K(\Delta\theta/L)^2 L_M \sim K(L_M/L)^2 L_M^{-1}$ per unit area of S.

This approach thus results in an enormous negative subsurface energy density as compared to any standard macroscopic value. Indeed, the ratio is $|f_{13}/f_0| \sim (L/L_M)^2 \gg 1$, if we suppose elastic constants K_{13} and the Frank constants K to be of the same order of magnitude as predicted recently [18]. The factor $(L/L_M)^2$ is so large that the nematic phase—in particular the freely suspended nematic phase—must spontaneously increase its surface area because its "surface tension" is negative. Then the state of a freely suspended nematic drop would not be equilibrium and the drop would be elongated into a thin rope and so on. We know, however, that such effects do not occur.

To a certain extent the authors of Refs. [8,10,11] realize the inconsistency of this approach [10], leading to such exotic predictions for nematic liquid crystals. However, there is still no other approach that is at least formally consistent.

Rather than face this problem, Hinov [9,12] proposed a postulate that the director must satisfy the Euler-Lagrange equations corresponding to the functional F_2. Of course, this postulate results in bounded deformations; however, F_2 has its own minimum for each function family, and the exclusive role of the Euler-Lagrange equations for F_2, containing the K_{13} term, is by no means clear.

Thus, the problem of the K_{13} term has not reached a level where it can be solved, either experimentally by measuring the elastic constant K_{13}, or by discovering an effect caused by the K_{13} term alone. In this context, it is interesting to note that sometimes, depending on the specific problem, the situation impels researchers to accept one of two diametrically opposite points of view. Thus theoretical considerations imply the existence of strong subsurface director deformations [11], whereas the necessity of carrying out measurements of K_{13} leads to the acceptance of the heuristic point of view that the director must satisfy the Euler-Lagrange equations for F_2 [19].

The problem of the K_{13} term also calls into question investigations of the effects associated with the K_{24} term in the FE, making them heuristic in the best case. Indeed, it is difficult to find a situation when the K_{13} term can be ignored while the K_{24} term plays an important role. The problem is that both surfacelike terms come into play in the same situations: either in geometries with a sufficiently large surface-to-volume ratio or when there are singularities in the director distribution (defects). At the same time, while the K_{13} term can contribute to the FE in any geometry, the K_{24} term is identically equal to zero if the director depends on a single Cartesian coordinate. Thus physically the problem of the K_{13} and K_{24} terms cannot generally be divided into two independent ones.

Along with the surfacelike terms in the bulk part of the FE, derivative-dependent terms can be introduced in the expression of the anchoring energy. Some surface energy densities widely quoted in the literature are

$$f_{\mathrm{RP}}=\tfrac{1}{2}W_{\mathrm{RP}}\sin^2(\theta-\bar{\theta}) , \tag{5}$$

$$f_{\mathrm{DVP}}=\tfrac{1}{2}W_{\mathrm{DVP}}\sin[2(\theta-\bar{\theta})]\theta' , \tag{6}$$

$$f_M=\tfrac{1}{4}W_M\sin^2[2(\theta-\bar{\theta})]\theta'^2 , \tag{7}$$

which are referred to as the Rapini-Papoular [20], Dubois-Violette and Parodi [21], and Mada [22] terms, respectively. Here θ is the angle between $\mathbf{n}$ and the normal $\boldsymbol{\nu}$ to S, $\theta-\bar{\theta}$ is the angle between $\mathbf{n}$ and the easy direction $\mathbf{e}$ on S, and the prime denotes the derivative of θ along $\boldsymbol{\nu}$.

Evidently, the problem of the derivative-dependent terms in the surface part of the FE must also incorporate the anchoring terms (5)–(7). In this paper we solve this problem on the phenomenological level. This corresponds to a macroscopic description of liquid crystals and maximally employs the features of the realistic nematic phases which appear in the Landau theory. As a result, the problem is reduced to the experimental measurement of the constants K_{11}, K_{22}, K_{33}, K_{24}, K_{13}, and W_{RP}. No additional phenomenological constants enter the theory.

Generally speaking, the problem of the surfacelike K_{13} term in the nematic FE has three principal aspects: microscopic, the inclusion of the K_{13} term in the macroscopic description, and, at last, the observable consequences of the inclusion. Respectively, this paper, devoted to the second aspect, belongs to a series consisting of three papers. In the first one [18] the microscopic procedure of the computation of the elastic constant K_{13} is shown to be unambiguous, and K_{13} itself and the usual Frank constants are of the same order of magnitude. The third paper [23] presents an effect due to the K_{13} term alone. The computation performed in [18] confirms that the values of K_{13} necessary for this effect to exist are not exotic; the effect itself is a direct corollary of the phenomenological theory worked out in the present paper.

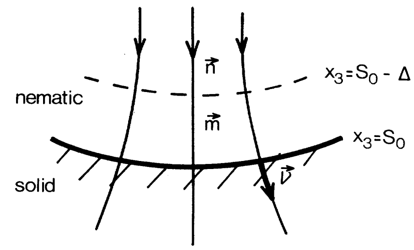

FIG. 1. Part of the nematic-solid substrate interface S which coincides with the coordinate surface $x_3=S_0$. The coordinate lines x_1 and x_2 lie on the surface x_3=const, while the coordinate lines x_3, whose directions are indicated by arrows, are perpendicular to them; $\boldsymbol{\nu}$, the unit external normals to the nematic surface S, are directed along these x_3 lines. In the volume inside the surface $x_3=S_0-\Delta$ located an arbitrary distance Δ (along the x_3 lines) from S, an arbitrary director distribution $\mathbf{n}$ is fixed; $\mathbf{m}$ is the distribution (12), (13) satisfying the boundary condition $\mathbf{m}(x_3=S_0-\Delta)=\mathbf{n}(x_3=S_0-\Delta)$ on the inner surface $x_3=S_0-\Delta$ of the subsurface Δ layer.

II. UNBOUNDEDNESS OF THE FREE-ENERGY FUNCTIONAL F_2 FROM BELOW FOR $K_{13}\neq 0$

To formulate the problem of derivative-dependent terms in the surface part of the functional FE one first of all has to understand the mathematical nature of strong subsurface deformations predicted by Barbero and Oldano [8] and considered in detail subsequently [8,10,11,13,16,17].

The crucial question in this context is to understand why, when both K_{13} and K_{24} terms introduce the director derivatives in the surface part of the FE, the K_{24} term does not lead to any paradoxes and exotic deformations, while the K_{13} term does cause problems? The answer is that, for any arbitrary surface S of a nematic sample, the K_{24} term f_{24} (4) contains only derivatives $\partial_{\parallel}n$ in the direction tangential to S and does not contain derivatives $\partial_{\perp}n$ along the normal directions; whereas the K_{13} term always contains the director derivatives $\partial_{\perp}n$ normal to S. This result, which is of a crucial importance in the context of the paper, as well as the derivation of a direct variational procedure for the FE functional (2), containing only the K_{24} term, are obtained in the Appendix.

Now we shall show that it is just singularity of the normal derivatives $\partial_{\perp}n$ on S which allows an unbounded decrease in the value of F_2. The result is that the functional F_2 has no minimum for any nonzero K_{13}.

Thus we want to show here that the presence of the K_{13} term always leads to an infinite negative value of F_2. "Always" means that it takes place for nematic phases with arbitrary surface S when arbitrary boundary condition for the director is fixed at an arbitrary distance Δ from the surface (Fig. 1). Since S in the general case is not planar, it is appropriate to introduce a curvilinear coordinate system (x_1,x_2,x_3) with metric tensor g_{ij} in such a way that the nematic surface S coincides with the coordinate surface $X_3=\text{const}=S_0$. Then x_1 and x_2 are the coordinates on S, and the outer normal $\boldsymbol{\nu}$ is directed along the coordinate line x_3: $\boldsymbol{\nu}=(0,0,1)$. In these coordinates, the differentials of the area of S and the volume are given by $dS=\sqrt{g_{11}g_{22}}dx_1dx_2$ and $dV=\sqrt{g_{33}}dx_3dS$, respectively. Now, all the differential operators must be written in terms of these curvilinear coordinates. Introducing the notation $\partial_i n_j=\partial n_j/\partial x_i$, $g=g_{11}g_{22}g_{33}$, using a unit antisymmetric tensor $\epsilon_{ijk}(i,j,k$ take the values 1,2,3) and implying the summation over similar subscripts, we have [24]

$$(\nabla\cdot\mathbf{n})=\frac{1}{\sqrt{g}}\partial_i(n_i\sqrt{g/g_{ii}})\ , \tag{8}$$

$$(\nabla\times\mathbf{n})_i=\epsilon_{ijk}\sqrt{g_{ii}}\partial_j(\sqrt{g_{kk}}n_k) \quad \text{(no summation over } i\text{)}\ , \tag{9}$$

$$f_{13}=K_{13}\frac{n_3}{\sqrt{g}}\partial_i(n_i\sqrt{g/g_{ii}})\ . \tag{10}$$

Let us consider the subsurface layer $S_0\geq x_3\geq S_0-\Delta$ with the arbitrary boundary condition $\mathbf{n}(x_1,x_2,x_3=S_0-\Delta)=\mathbf{v}(x_1,x_2)$ on its inner boundary $x_3=S_0-\Delta$, all the derivatives of the function $\mathbf{v}$ being finite. Such a boundary condition can be associated with an arbitrary director distribution in the volume. The FE F_Δ of this layer is given by the integral over its volume plus the anchoring energy which at this stage is assumed to be a functional on $\mathbf{n}$ only (∂n-dependent anchoring will be considered in the next section):

$$F_\Delta=\int_{S_0-\Delta}^{S_0}dx_3\int_S dS\sqrt{g_{33}}f_F+\int_S dS[f_{13}+f_{24}+f_A(\mathbf{n})]\ , \tag{11}$$

where $f_A(\mathbf{n})$ is the surface density of the anchoring energy.

In order to prove that F_Δ is not bounded from below, it is sufficient to find in the layer a director distribution $\mathbf{m}(\mathbf{x})$ which satisfies the boundary condition $\mathbf{m}(x_1,x_2,x_3=S_0-\Delta)=\mathbf{n}(x_1,x_2,S_0-\Delta)=\mathbf{v}(x_1,x_2)$ and leads to $F_\Delta\{\mathbf{m}\}\rightarrow-\infty$. Let the third component of the director distribution $\mathbf{m}(\mathbf{x})$ in the layer be the function

$$m_3=\beta(S_0-x_3)^\alpha-\beta\Delta^\alpha+v_3(x_1,x_2)\ , \tag{12}$$

which identically satisfies the boundary condition on the surface $x_3=S_0-\Delta$; α and β are constants, $\frac{1}{2}<\alpha<1$. Suppose the second component of $\mathbf{m}$ coincides with its value for $x_3=S_0-\Delta$, so that

$$m_2(x_1,x_2,x_3)=v_2(x_1,x_2)\ ,$$
$$m_1(\mathbf{x})=\pm\sqrt{1-m_2^2(\mathbf{x})-m_3^2(\mathbf{x})}\ , \tag{13}$$

where the sign of m_1 can be obtained from the continuity condition of n_1 for $x_3=S_0-\Delta$.

We see from (12) that $|\partial_3 m_3|\to\infty$ on S, i.e., for $x_3=S_0$, the director itself being finite. Let us separate the infinite director derivatives. The following behavior of the derivatives can be found from (12) and (13) for $x_3\to S_0$:

$$|\partial_3 m_3|\propto|\alpha\beta(S_0-x_3)^{\alpha-1}|\to\infty\ ,\quad \partial_3 m_2=0\ ,$$
$$|\partial_3 m_1|=\left|\frac{-m_3\partial_3 m_3}{m_1}\right|\to\infty\ , \tag{14}$$
$$|\partial_3 m_1|<\infty\ ,\quad |\partial_2 m_j|<\infty\ .$$

Thus only $\partial_3 m_3$ and $\partial_3 m_1$ are infinite and both behave as $\alpha\beta(S_0-x_3)^{\alpha-1}$ for $x_3\to S_0$. As it follows from (8), (9), and (1) these derivatives contribute both to the volume and surface parts of F_Δ. However, it is easy to see that the resulting singularity in the volume integral is integrable. The volume integral is thus finite:

$$\int dx_3\bar{K}\alpha^2\beta^2(S_0-x_3)^{2\alpha-2}\propto\alpha^2\beta^2\frac{(S_0-x_3)^{2\alpha-1}}{2\alpha-1}\to 0\ , \tag{15}$$

for $x_3\to S_0$. Here $\bar{K}$ is a finite factor which depends on $K_{11},K_{22},K_{33},\mathbf{n}$, and finite $\partial\mathbf{n}$. The surface density f_{24} from Eq. (4) is shown in the Appendix to contain no director derivatives along the directions normal to the surface. Thus f_{24} does not contain the only infinite derivative $\partial_3 n$ and, hence, the f_{24} contribution to the FE layer F_Δ is finite. Then, separating the infinite part of f_{13} (8), we find the infinite part of the K_{13}-term contribution to be

$$F_\Delta=\int_S dS\,K_{13}\left[m_3\frac{1}{\sqrt{g_{33}}}\partial_3 m_3\right](x_3=S_0)$$
$$\propto K_{13}\alpha\beta(S_0-x_3)^{\alpha-1}\ , \tag{16}$$

for $(S_0-x_3)\to 0$. We see that $|F_\Delta|\to\infty$ and can be made negative, whatever the sign of K_{13}, by the choice of sign of the factor β: if $K_{13}\beta<0, F_\Delta\to-\infty$.

III. RESTRICTION OF DEFORMATIONS AND HIGHER-ORDER ELASTICITY

Thus, the strong subsurface deformations normal to S result in the unbounded drop in F_2 both in the simplest cases considered in Refs. [8,10] and for an arbitrary nematic geometry. However, this picture is formal both mathematically and physically.

From the mathematical point of view, the unboundedness of the F_2 from below means that it has no minimum while, from the physical one, these strong deformations are in accordance neither with our ideas of the nematic phase nor with the assumptions about the weakness of any deformations underlying the derivation of the very functional F_2 and which must be verified *a posteriori*. The first mathematical inconsistence can be removed from the theory by adding to F_2 some term R_h of the order higher than F_2 in the operator ∂, which bounds the FE from below and hence ensures the existence of $\min(F_2+R_h)$. For example, Barbero, Madhusudana, and Oldano [11] propose the form $R_4=\int P_4(\partial n)^4 dV$, where P_4 is some fourth-order elastic constant (qualitatively similar terms, which all can be denoted as R_4, were introduced by Sparavigna, Komitov, and Strigazzi [16]). Evidently, both the total FE $F=F_2+R_4$ and the director derivatives are now bounded. But to make the theory physically consistent is much more difficult. Indeed, though the deformations become finite in this approach, their values are still too high, $\partial_\perp n\sim 1$ on S [11,13,16] while it must be of the order $\partial_\perp n\sim L_M/L\ll 1$ in the nematic phase [1,26]. It is clear that such a theory predicts that the scales L_M and L coincide which, generally speaking, makes a macroscopic description impossible (the less formal nonphysical consequences given in the Introduction should be added to this reasoning).

A further question arises as to whether one or several terms of fourth order must be introduced in R_4. Such an ambiguity could be removed by taking into account in R_4 all possible terms of the fourth order (there are, however, 35 such terms [1]). It is clear that this approach just complicates the problem, without solving it. Indeed, the total contribution of any order contains, along with the bulk elastic terms (with unknown elastic constants), alternate divergence terms, which also are unbounded from below. For example, at order ∂^4 there is a term $\nabla\cdot[\mathbf{n}\Delta(\nabla\cdot\mathbf{n})]$, which introduces the third-order derivative $\partial_\perp^3 n$ in the surface part of the FE. Just as the K_{13} term is unbounded from below, this term removes the lower bound of the sum F_2+R_4, which again has no minimum. Then, in order to restrict the value of this term, one must take into account sixth-order terms, among which, however, the term $\nabla\cdot[\mathbf{n}\Delta\Delta(\nabla\cdot\mathbf{n})]$ exists, and so on. Thus, it is impossible to solve the problem by introducing new elastic terms up to any finite orders.

Nevertheless, the problem of the K_{13} term must reduce to finding the *appropriate* regularization term R_∞ which can be attributed to the contribution of *all* higher-order terms to the nematic FE. We shall formulate this problem in detail in the next section.

IV. PHENOMENOLOGICAL APPROACH TO THE PROBLEM OF THE REGULARIZATION TERM R_∞

Mathematically, the K_{13} problem follows from two contradictory assertions: (1) for arbitrary nematic geometry, the free energy F_2 is unbounded from below for any $K_{13}\neq0$ (Sec. II), and (2) all microscopic theories of nematics predict $K_{13}\neq0$ (for example, see Refs. [11,15,18] and references therein).

It follows from assertion (1) that F_2 has no minimum for $K_{13}\neq0$ and the normal derivatives $|\partial_\perp n|\to\infty$ for $\mathbf{x}\in S$ (infinite deformations). However, the phenomenological theory of nematic liquid crystals is analogous to a Landau theory of phase transitions. One cannot consider arbitrary consequences of such a theory. Rather, such a theory essentially employs the idea of a specific ground state and permits the description only of weak deviations of the order parameter from this state. In our case, this corresponds to the assumption that all possible deformations in the nematic liquid crystal are weak, $|\partial n|\ll1$. The real task is how to preserve the standard phenomenological approach, and at the same time to remove the exotic formal consequences of the theory. We shall show below that there exists a unique solution of the problem within the framework of a consistent phenomenological approach.

Let us formulate the requirements for possible nematic states and the functional R consistent both with generally accepted ideas and the experimental data:

(i) Deformations in a nematic liquid crystal are weak, $|\partial n|\sim|L_M/L|$ (which allows spontaneous weak deformations in contrast to the requirement that $\partial n=0$ without any external forces).

(ii) A satisfactory theory of a nematic liquid crystal must employ only the functional F_2 quadratic in the operator $\partial\sim L_M/L$. This means that though the higher-order terms F_{2K} for $K=2,3,\ldots$ in principle can play an important *mathematical* role in the theory, they must not enter explicitly the observable quantities, i.e., $|F_2|\gg|R_\infty|$ where $R_\infty=\sum_{K=2}^{\infty}F_{2K}$. It is clear that (ii) can be satisfied only due to (i) since it follows from (i) that $F_{2K}\sim(L_M/L)^{2K}$ [1,13,26].

For example, R of the form $\int P_4(\partial^4 n)dV$ [11,16] contradicts both (i) ($|\partial n|\sim1$) and (ii) ($|F_2|\sim|R|$ and $\mathbf{n}$ essentially depends on P_4).

If a finite number of terms in R does not solve the problem, the only possibility which remains is that R in the form of the infinite sum R_∞ satisfies all the requirements formulated above. It is clear that R_∞ cannot be obtained explicitly. Nevertheless, there are in fact only two possibilities: either $K_{13}=0$, or R_∞ behaves in the required fashion; otherwise (i) and (ii) are not satisfied. Therefore, the problem can be formulated as follows: (a) to determine which behavior of R_∞ is required to satisfy (i) and (ii); (b) to show, that, in principle, such behavior does not contradict the definition of R_∞; (c) to find the minimization procedure for the functional $F=F_2+R_\infty$ and to show that this procedure does not require information about R_∞ more detailed than in (a) above.

Before performing this program, in the next section we consider the derivative-dependent terms in the anchoring energy. We shall see that this will throw light on the K_{13} problem and give a very useful example of an infinite sum possessing all the features required of R_∞. Of course, the problem of the terms (5)–(7) in the anchoring energy is also important in itself.

V. DERIVATIVE-DEPENDENT TERMS IN THE ANCHORING ENERGY

If each derivative sign in the bulk density given by Eq. (1) is proportional to the small parameter L_M/L, then the anchoring energy contains no scale parameters explicitly. Therefore, ∂n-dependent terms in Eqs. (6) and (7) were introduced in the anchoring energy only for symmetry reasons and no magnitude hierarchy in the derivative powers occurs in the approach. We propose now a simple physical idea which enables us to introduce the derivative-dependent terms in the anchoring energy naturally and estimate how small they are.

On a molecular length scale there is an interaction between the nematic molecules and a surface field penetrating inwards to some small depths L_S. This physical idea underlies the introduction of the phenomenological quantity known as the anchoring energy. The anchoring energy acts solely at the surface and has permitted the successful interpretation of experimental results. This idea that the anchoring energy results from the bulk interaction with the external field produced by the surface was articulated most explicitly by Sluckin and Poniewierski [27], by Sen and Sullivan [28], and by Osipov [29], and will be employed in what follows.

It is known that the surface field directs the nematic liquid-crystal (NLC) molecules on the surface along a certain easy direction $\mathbf{e}$. This field can be considered as a vector, $\boldsymbol{\psi}=\psi(\mathbf{x})\mathbf{e}$, in the case of an azimuthally isotropic surface which is considered here only to simplify the formulas. Its magnitude decreases rapidly towards the normal-to-S direction so that $\int_0^{L_S}\psi^2 z^K dz\simeq\int_0^\infty\psi^2 z^K dz$, where $z=|x_3-S|$. The interaction energy density can be written as

$$f_\psi=-\tfrac{1}{2}W_2(\mathbf{n}\cdot\boldsymbol{\psi})^2+W_4(\mathbf{n}\cdot\boldsymbol{\psi})^4+\cdots\ . \tag{17}$$

If $\bar\theta(x_1,x_2)$ is the angle between $\boldsymbol{\nu}$ and $\mathbf{e}$, then the quadratic term has the form (with the accuracy of an $\mathbf{n}$-independent constant)

$$f_{\psi,2}=\tfrac{1}{2}W_2\psi^2(\mathbf{x})\sin^2[\theta(\mathbf{x})-\bar\theta]\ , \tag{18}$$

where $W_2>0$. Now the total FE is given by the sum $F=F_2+F_{S,2}$ where

$$F_{S,2}=\int dV f_{\psi,2}=\int dS\int_0^\infty dz\sqrt{g_{33}(x_1,x_2,z)}f_{\psi,2}\ ; \tag{19}$$

the elastic constant K_{13} is taken to be zero in F_2 in this section. Under this condition, the form of Eq. (18) ensures that $f_{\psi,2}$ is bounded from below, and hence F is also bounded from below. The functional F is minimized by solutions of Euler-Lagrange equations; these differ from the Euler-Lagrange equations of the functional F_2 alone only in a thin subsurface layer of thickness L_S.

Equation (18) represents the surface–nematic-phase interaction as a standard bulk effect. However, we would like to treat the energy density given by Eq. (18) traditionally, i.e., as a purely surface term. Of course, these two representations, bulk and surface, must be equivalent, i.e., they must lead to the same families of extremals for F, which can in principle differ only in the layer of thickness of order L_S near S. However, here they must actually coincide in order to give the same value of the free energies. One can pass to the "surface" representation in the following way. Expanding $\sin^2$ in (18) in power series of z near S given by $z=0$, we find the surface density $f_{S,2}(x_1,x_2)=\int_0^\infty dz\sqrt{g_{33}}f_{\psi,2}$ to be

$$f_{S,2}(x_1,x_2)=\tfrac{1}{2}W_2\left\{\left[\int_0^\infty \psi^2\sqrt{g_{33}}dz\right]\sin^2(\theta_0-\bar{\theta})+\left[\int_0^\infty \psi^2\sqrt{g_{33}}z\,dz\right]\sin[2(\theta_0-\bar{\theta})]\frac{d\theta_0}{dz}\right.$$
$$\left.+\tfrac{1}{2}\left[\int_0^\infty \psi^2\sqrt{g_{33}}z^2dz\right]\left[2\cos^2[2(\theta_0-\bar{\theta})]\left[\frac{d\theta_0}{dz}\right]^2+\sin[2(\theta_0-\bar{\theta})]\frac{d^2\theta_0}{dz^2}\right]+\cdots\right\}, \qquad (20)$$

where $\theta_0=\theta(z=0)$, $d\theta_0/dz=(d\theta/dz)(z=0)$. Since $\int_0^\infty\psi^2\sqrt{g_{33}}z^kdz\sim L_S^k\int_0^\infty\psi^2\sqrt{g_{33}}dz\sim L_S^{k+1}$ and L is the scale of θ changes, in fact (20) turns out to be the expansion in the power series of the small parameter L_S/L. The first term in (20) coincides with the surface Rapini-Popoular term [20] $f_{\rm RP}$ if the notation $W_{\rm RP}=W_2\int_0^\infty\psi^2\sqrt{g_{33}}dz$ is introduced; the second term reproduces the one $f_{\rm DVP}$ introduced by Dubois-Violette and Parodi [21]. The latter is (L/L_S) times smaller than $f_{\rm RP}$. In the next order of smallness $\sim f_{\rm RP}(L_S/L)^2\sim f_{\rm DVP}(L_S/L)$, the term $\cos^2[2(\theta_0-\bar{\theta})](d\theta_0/dz)^2$ exists, which coincides with Mada term [22] f_M with the accuracy of the term const$(d\theta_0/dz)^2$ allowed by the symmetry, and also the term $\sin[2(\theta_0-\bar{\theta})]d^2\theta_0/dz^2$ exists. The terms of the order of $f_{\rm RP}(L_S/L)^3$ and higher are omitted in (20) but of course they can be easily calculated. The term $W_4(\mathbf{n}\cdot\boldsymbol{\psi})^4$ in (17) can be written in the similar form, too.

The quantity $f_{S,2}(x_1,x_2)$ (20) represents the surface density of the surface–nematic-phase interaction and its contribution $F_{S,2}=\int dSf_{S,2}$ is given by a surface rather than by a bulk integral (19). Thus, the formula (20) gives the "surface" representation of the surface–nematic-phase interaction energy.

We emphasize that passing from the bulk (19) to the "surface" representation of Eq. (20) is possible only as a result of the smallness of L_S. If L_S is comparable with L, then $|x_3-S_0|$ must be taken for the upper limit in the integrals entering (20). In that case the function on the left-hand side of Eq. (20) depends on x_1,x_2, and also on x_3; the Euler-Lagrange equations of the functionals F_2 and $F_2+F_{S,2}$ differ in the bulk region which cannot be considered as a subsurface region, and hence the "surface" and bulk representations, Eqs. (19) and (20), of the surface–nematic-phase interaction are no longer equivalent.

Thus, Eq. (20) can be thought of as a valid simplification of Eq. (18) only if the condition $L_S/L\ll 1$ is satisfied. Of course, normally this is indeed the case. Then each term of the series (20) has the form const$(L\partial n)|_{z=0}^k(L_S/L)^k$ where const~ 1, $|L\partial n|\sim 1$ by the L-scale definition, and each surface derivative in the anchoring energy is proportional to a small factor (L_S/L) just as each bulk derivative is proportional to L_M/L. Thus, we obtain a hierarchy of contributions of derivative-dependent terms in the anchoring energy which now can be classified by order of magnitude.

Since each power of ∂ introduces a small factor in the anchoring energy, the minimization problem for the functional $F=F_2+F_{S,2}$ can be solved in the form of a power series of this factor by means of perturbation theory.

In the lowest-order approximation the only term contributing to the anchoring energy is the Rapini-Popoular term $F_{\rm RP}=\int f_{\rm RP}dS$. In this approximation the extremal family of the FE, which is equal to $F_2+F_{\rm RP}$, is the solution of the Euler-Lagrange equations for the functional F_2. The next terms of the series (20) give small corrections of the order of (L_S/L), $(L_S/L)^2$, and so on, and thus play no practical role as compared with the first approximation.

Let us look at the formula (20) from another point of view. Since $f_{\psi,2}$ in Eq. (18) is bounded from below, $f_{S,2}=\int dz\sqrt{g_{33}}f_{\psi,2}$ is bounded and, in this respect, the infinite sum (20) possesses suitable behavior. Let us try to truncate this series and to restrict it to finite powers $\bar{k}$ of ∂. If one formally uses such a sum $f_{S,2}^{(\bar{k})}$ in order to determine the director distribution, the same difficulties appear as appear in the problem of the K_{13} term. Indeed, for any $\bar{k}$ the surface part $F_S^{(\bar{k})}$ of the FE contains the normal-to-S derivative of $\bar{k}$th order that leads to its unboundedness when the FE if formally minimized. If we did not know about the equivalence between the infinite sum (20) and the expression (19), again, as in the case of the K_{13} term, we would restrict the sum by $\bar{k}=1$ and obtain the strong subsurface deformations ($|d\theta_0/dz|\to\infty$) and so on. This shows that it is impossible to restrict the sum $R_{\bar{k}}$ to any finite number of terms but that it is nevertheless possible that the infinite sum R_∞ possesses the necessary behavior. What is important here is that in order to find the distribution with accuracy $(L_S/L)^2$ it is not necessary to know all the higher terms of the series (20). To demonstrate this further, let us consider an example which is extremely close to the K_{13} problem and restrict the sum to $\bar{k}=1$:

$$f_{S,2}^{(1)}=\tfrac{1}{2}W_{\rm RP}\sin^2(\theta_0-\bar{\theta})+\tfrac{1}{2}W_{\rm DVP}\theta_0'\sin[2(\theta_0-\bar{\theta})]\ . \qquad (21)$$

Formally, (21) results in $|\theta_0'|\to\infty$ on S, however, we know that the sum of all the higher-order terms of the series (20) bounds the FE from below so that $\theta'\sim L^{-1}$ in the ground state. Then, since $\theta' W_{\rm DVP}\sim(L_S/L)^2\ll W_{\rm RP}\sim L_S/L$, the FE, corresponding to (21), contains in the first approximation just the first term from (21), and its minimum can be found by solving the Euler-Lagrange equations of the functional F_2. The role of all higher terms is reduced to the restriction of the functions, upon which $\min F^{(1)}$ is sought, to the family of solutions of the Euler-Lagrange equations for the functional F_2. The terms of the anchoring energy containing the derivatives give contributions which are L_S/L, $(L_S/L)^2$, and so on, times smaller than the Rapini-Popoular term and can be taken into account as perturbations.

VI. STRUCTURE OF THE REGULARIZATION TERM R_∞ AND THE MINIMIZATION PROCEDURE

We know from the previous sections that the regularization term R_k is of infinite sum form, i.e., $k=\infty$. We have also seen, *both* that this sum R_∞ can ensure that the theory satisfies the basic requirements (i) and (ii) *and* ignoring the specific form of R_∞ cannot be regarded as a serious obstacle. So we pass to the solution of the problem formulated in point (a) from Sec. III, which is to determine the necessary behavior of R_∞.

We have shown in Sec. II and in the Appendix that the nematic FE containing the K_{13} term can be written in the form

$$F_2=F_b+K_{13}\int_S dx_1dx_2\sigma\xi \ , \tag{22}$$

where F_b is the part of F_2 bounded from below, $\xi(\mathbf{x})=\boldsymbol{\nu}\partial(\boldsymbol{\nu}\cdot\mathbf{n})/\partial\mathbf{x}$ is the derivative of the director normal-to-S component along the normal $\boldsymbol{\nu}$ to S (in the notation of Sec. II $\xi=\partial n_3/\partial x_3$), $\sigma(\mathbf{x})$ is a nonsingular function determined on S [see formula (A14)]. For F_2 to be bounded from below, the surface density τ of the function R_∞ also must depend on ξ. Evidently, it must be such that the function

$$p(\xi)=K_{13}\sigma(\mathbf{x})\xi(\mathbf{x})+\tau(\xi(\mathbf{x})) \tag{23}$$

must be bounded from below at each point $\mathbf{x}\in S$ and, hence, must have a minimum for some value $\xi_m(\mathbf{x})$ of $\xi(\mathbf{x})$. According to (i), all the deformations including ξ are weak, i.e., $|\xi_m|\ll 1$; according to (ii), the high-order terms in the FE are very small, i.e., $|K_{13}\sigma\xi|\gg|\tau(\xi)|$ for $|\xi|<|\xi_m|$ at each point $\mathbf{x}\in S$. The only dependence $\tau(\xi)$, that satisfies the requirements, and the relevant function $p(\xi)$ are shown qualitatively in Fig. 2 under the assumption that $K_{13}\sigma<0$ (for $K_{13}\sigma>0$, one simply has to plot p and τ for negative ξ). It is clear that for $|\xi|<|\xi_m|$, where $|\xi_m|\sim L_M/L\ll 1$, $|\tau|\ll|p|$, so that the inequality $|K_{13}\sigma\xi|\gg|\tau|$ (or $|F_2|\gg|R_\infty|$) is satisfied. For $|\xi|\sim|\xi_m|$, τ increases steeply, as a result $|\xi|$ is bounded by the value $|\xi_m|$. It is clear that the regime of values $|\xi|>|\xi_m|$ is never reached in the system, since it does not correspond to a minimum of the FE. Moreover, the value $|\xi_m|$ itself can be reached only in the case when all elastic constants other than K_{13} vanish. Since this is impossible, the normal derivatives ξ on S in a real nematic liquid crystal are always smaller than ξ_m, and the value ξ_m itself does not enter any observable quantities. Thus,

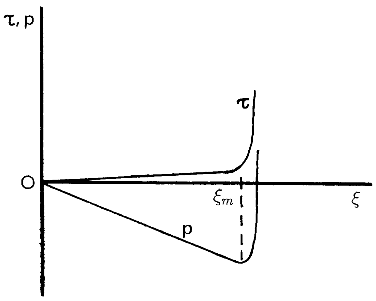

FIG. 2. Qualitative dependences of the surface density τ of the regularization term R_∞ and the total surface density p of the nematic FE on the value ξ of a normal-to-S derivative. If $|\xi|<|\xi_m|$, $|\tau|\ll|p|\cong|K_{13}\sigma\xi|$, and the total contribution of the higher-order elasticity R_∞ is negligible, $|R_\infty|\ll|F|\cong|F_2|$. The distortion range $|\xi|\geq|\xi_m|$ for which $|\tau|\sim|p|\sim|K_{13}\sigma\xi|$ corresponds to a high value of the free energy and thus is never realized in the system.

the role of the quantity ξ_m is that the system senses the energetic unfavorableness of the state with $|\xi|>|\xi_m|$, and strong deformations do not occur.

The form of $\tau(\xi)$ given in Fig. 2 can be easily interpreted. The standard expressions for the elastic constants are derived by means of the expansion in the power series of infinitesimal deviation $\delta\mathbf{n}$ from the state $\mathbf{n}=\text{const}$ [1,26]. Finite $\delta\mathbf{n}$ renormalizes these expressions. Then a steep increase of $\tau(\xi)$ for $|\xi|\sim|\xi_m|$ can mean a corresponding decrease in the absolute value of the renormalized constant K_{13} when $|\xi|$ becomes sufficiently large.

Now let us pass to point (c) of Sec. III and find the procedure minimizing the functional $F=F_2+R_\infty$. F is bounded from below and hence has a minimum. Given that $|R_\infty|\ll|F_2|$ for $|\xi|<|\xi_m|$, the minimization of F_2+R_∞ for arbitrary ξ with the accuracy of order $(L_M/L)^4$, which is the lowest order in the series R_∞, is equivalent to minimizing the functional F_2 under the restriction $|\xi|<|\xi_m|$:

$$\min_{\forall\xi}(F_2+R_\infty)\Longleftrightarrow\min_{|\xi|<|\xi_m|}F_2 \ . \tag{24}$$

For $|\xi|<|\xi_m|$ the functional F_2 (1) is minimum on some family of functions $\mathbf{n}_c$ where c corresponds to a parametrization of that set of functions. Since $\min(A+B)\geq\min A+\min B$, one has to seek such $\mathbf{n}_c$ that minimizes the bulk $F_{2,V}$ and the surface $F_{2,S}$ contributions to the functional $F_2=F_{2,V}+F_{2,S}$ separately. The bulk part $F_{2,V}$ is minimum on the family of solutions $\boldsymbol{\psi}(\mathbf{x},c)$ of the Euler-Lagrange equation corresponding to $F_{2,V}$. If this family is such that the normal derivative $\xi(\mathbf{x},c)=\partial_\perp\psi_\perp(\mathbf{x},c)$ can take any value $\xi'\in(-|\xi_m|,|\xi_m|)$ at each point $\mathbf{x}$ of the surface, then the condition $|\xi|<|\xi_m|$ in (24) does not impose additional restrictions on the family $\mathbf{n}_c$. Equivalently, suppose $\partial_\perp\psi_\perp(\mathbf{x},c)$ as a function of c cannot run over the whole interval $(-|\xi_m|,|\xi_m|)$. Now $\min(F_{2,V}+F_{2,S})$ may occur on another family, permitting a decrease of $F_{2,S}$ (i.e., the K_{13} term), since ξ can now be taken in the whole interval

$(-|\xi_m|,|\xi_m|)$, rather than in a certain part of it.

Thus, we have proven the following assertion: $\min_{|\xi|<|\xi_m|}F_2$ occurs on the solutions $\mathbf{n}_c=\boldsymbol{\psi}(\mathbf{x},c)$ of the Euler-Lagrange equation of F_2 if the solution c of the equation $\partial_\perp\psi_\perp(\mathbf{x},c)=\xi$ exists for any $\mathbf{x}\in S$ and any $|\xi|<|\xi_m|$.

Of course, here c consists of numerical parameters only in the simplest cases. Generally speaking, it is made up of functions $c(\mathbf{x})$ corresponding to the arbitrariness of the solutions of partial differential equations. The case when the equation $\partial_\perp\psi_\perp(\mathbf{x},c)=\xi$ has no solution seems to be rather exotic so we shall not consider it.

In order to obtain $\mathbf{n}_c$ corresponding to $\min(F_2+R_\infty)$, one has first to find an arbitrary solution of the Euler-Lagrange equations of F_2, then to introduce it in the functional F_2, $F_2\{\mathbf{n}_c\}=P(c)$, and finally to minimize the function $P(c)$ (or functional) obtained with respect to c.

Let us consider the one-dimensional case for the simplest example. Then $\mathbf{n}=(\sin\theta,\cos\theta)$, $\theta=\theta(z)$, the sample has two surfaces S_1 $(z=-d/2)$ and S_2 $(z=d/2)$. The solution of the Euler-Lagrange equations is $\theta=\theta(z,c_1,c_2)$, its derivative $d\theta/dz=\theta'(z,c_1,c_2)$; two arbitrary constants c_1 and c_2 can be expressed in terms of the angles θ_1 and θ_2 between the z axis and $\mathbf{n}$ on S_1 and S_2, respectively. Introducing θ and θ' in the FE $F=\int f_F dV+\sum_{s=1}^2\int dS_s(f_{13}+f_A)$, where $f_{13}=K_{13}\nu_z\theta'\sin(2\theta)$, $\nu_{z,1}=-1$, $\nu_{z,2}=1$, $f_A=f_A(\theta)$, and minimizing the obtained function of θ_1 and θ_2 with respect to these angles, we find the equations which are usually referred to as the boundary conditions:

$$\frac{\partial f_F}{\partial\theta'}-\frac{\partial f_A}{\partial\theta}+K_{13}\theta'\cos(2\theta_1)+\tfrac{1}{2}K_{13}\sin(2\theta_1)\frac{d}{d\theta_1}\theta'=0\ ,\quad z=-d/2\ ,$$

$$\frac{\partial f_F}{\partial\theta'}+\frac{\partial f_A}{\partial\theta}+K_{13}\theta'\cos(2\theta_2)+\tfrac{1}{2}K_{13}\sin(2\theta_2)\frac{d}{d\theta_2}\theta'=0\ ,\quad z=d/2\ . \tag{25}$$

Equations (25) permit the evaluation of θ_1 and θ_2 (and hence, c_1 and c_2) and the solution of the problem of the director distribution in the one-dimensional case. These equations were obtained long ago [30]. However, the assumption that the director satisfies the Euler-Lagrange equations of F_2 (1) had a heuristic character, and, as we have already said, has been explicitly criticized [14] (see also Ref. [31]).

Thus, the phenomenological approach based on the main assumptions (i) and (ii) leads to the following conclusion. The nematic free energy can be expanded in differential operators; the quadratic term is just F_2. The director minimizing the total nematic free energy satisfies the Euler-Lagrange equations of this functional F_2. This permits a solution of the K_{13} problem experimentally, by measuring the elastic constant K_{13}. For such a measurement to be possible, one has to consider theoretically the effects in which this constant plays an important quantitative role. In particular, the most dramatic effects would be those whose very existence is impossible for $K_{13}=0$. One such effect is presented in Ref. [23].

VII. CONCLUSION

We have shown that the problem of the K_{13} term and derivative-dependent terms in the anchoring energy is associated with derivatives normal to the nematic surface. The K_{24} term never contains such derivatives and, therefore, does not give rise to such problems.

In a consistent phenomenological approach, the specific structure of the ground state and the assumption that its deformations are weak ($|\partial n|\ll 1$) are essential ingredients in the construction of the FE functional. However, formal minimization of the functional F_2 (1) for $K_{13}\neq 0$ results in inadmissible deformations $|\partial n|\sim 1$. In this case we formulated the problem as follows: is it possible both to introduce the K_{13} term in the nematic FE and to save the basic idea of the nematic phase? We have shown that there exists a single possibility: the infinite sum R_∞ of all the higher-order terms in the FE expansion in the power series of the differentiation operator ∂ bounds the deformation on the necessary level and, at same time, no information concerning their specific form enters the observable quantities within the accuracy accepted in the standard macroscopic theory of the liquid crystals. The problem of the derivatives in the anchoring energy gives us one possible exact and detailed example of such series. Such behavior of R_∞ *is equivalent* to the possibility of introducing the K_{13} term in the nematic FE. In this case the director distribution is determined by the Euler-Lagrange equations of the functional F_2 (1), quadratic in ∂. If R_∞ does not possess the features needed, then either $K_{13}=0$ or the crystal under consideration is not nematic. Inasmuch as the results of our theory can be compared with the experimental data the K_{13} problem reduces to the experimental measurement of K_{13}. If the experiment gives $K_{12}\neq 0$, one can state that R_∞ behaves adequately; if $K_{13}=0$, the question of R_∞ does not arise at all. Thus, in spite of our approach being in spirit much closer to the approach of Barbero and Oldano, the formal conclusion coincides with those proposed by Hinov [9] *a priori*: minimum of the nematic FE is determined by the Euler-Lagrange equations of the F_2 (1) (see, however, Ref. [31]).

To make the picture complete, the approach should be considered in which the macroscopic theory employing only the functional F_2 is used to derive some restrictions or relations concerning the values of the elastic constants. For example, the requirement of boundedness of F_2 from below results in the known restriction [25] $|K_{22}+K_{24}|\le 2K_{11}$ for K_{24} and $K_{13}=0$ [13] for K_{13}; the requirement $F_2\ge 0$ plus the assumption *a priori* that the Euler-Lagrange equations determine $\mathbf{n}$ result, according to the author of Ref. [12], in the equality $|K_{33}-K_{11}|=2K_{13}$. On the other hand, it is clear that any elastic constant value can be obtained only from the microscopic theory. This contradiction can be eliminated if one requires the sum F_2+R_∞ rather than F_2 to be bounded. As we saw, it is then possible to introduce a finite K_{13} in the nematic liquid-crystal theory. Similarly, the restriction for K_{24} quoted above is not necessary: if it does not take place, then an infinite sum of all the contributions to the FE of the orders higher than two is able to restrict the director derivatives along the directions tangential to the surface, which enter the K_{24} term (see the Appendix). Thus, in this case, too, the realistic constant can be found only either from experiments or from the microscopic theory.

As for the requirement $F_2 \geq 0$ [12], it is equivalent to the assumption that there are no (even weak) spontaneous deformations in the force-free nematic phase. We believe that the question of the existence of such a deformation, which is equivalent to knowing the specific values of all the elastic constants, must be solved experimentally. Thus, there is no basis for any relations between elastic constants other than the microscopic theory.

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APPENDIX

Here we shall show that for an arbitrary nematic surface S (i) the surface density f_{24} (4) of the K_{24} term does not contain the director derivatives along the directions normal to this surface; (ii) the surface density f_{13} (3) of the K_{13} term contains them; and it is just these which lead to the unboundedness of the FE F_2 (1) from below. Additionally we shall obtain the direct variational procedure for any bounded functional containing derivative-dependent terms in its surface part. Inasmuch as we deal with an arbitrary curved surface, it is useful to write f_{24} in curvilinear coordinates using the notation of Sec. II. The first term in f_{24} is, in fact, already quoted in (8):

$$(\boldsymbol{\nu}\cdot\mathbf{n})(\nabla\cdot\mathbf{n})=\frac{n_3}{\sqrt{g}}\partial_i\left[n_i\left[\frac{g}{g_{ii}}\right]^{1/2}\right] . \tag{A1}$$

Using (7), one can write the second term in f_{24} as

$$\boldsymbol{\nu}\cdot(\mathbf{n}\times\nabla\times\mathbf{n})=\frac{1}{\sqrt{g}}\nu_3\epsilon_{3jk}n_j\epsilon_{klm}\sqrt{g_{kk}}\partial_l(\sqrt{g_{mm}}n_m) . \tag{A2}$$

Let us separate the normal derivatives $\partial_3\mathbf{n}$ in (A2). To do this it is convenient to introduce the subscripts s,s' taking the values 1,2, while others take the values 1,2,3. Then we have

$$\begin{aligned}\boldsymbol{\nu}\cdot(\mathbf{n}\times\nabla\times\mathbf{n})&=\frac{1}{\sqrt{g}}\epsilon_{3ss'}n_s\epsilon_{s's3}\sqrt{g_{s's'}}\partial_3(\sqrt{g_{ss}}n_s)+\frac{1}{\sqrt{g}}\epsilon_{3ss'}n_s\epsilon_{s'3s}\sqrt{g_{s's'}}\partial_s(\sqrt{g_{33}}n_3)\\&=\left[\frac{g_{22}g_{11}}{g}\right]^{1/2}(n_1\partial_3n_1+n_2\partial_3m_2)+J_S=-\left[\frac{g_{22}g_{11}}{g}\right]^{1/2}n_3\partial_3n_3+J_S .\end{aligned} \tag{A3}$$

When deriving the last equality, $\partial_3\mathbf{n}^2=0$ is used; J_S contains only director derivatives along the x_1 and x_2 directions:

$$\sqrt{g}J_S=n_1^2\sqrt{g_{22}}\partial_3\sqrt{g_{11}}+n_2^2\sqrt{g_{11}}\partial_3\sqrt{g_{22}}-(n_2\sqrt{g_{11}}\partial_2+n_1\sqrt{g_{22}}\partial_1)(\sqrt{g_{33}}n_3) . \tag{A4}$$

Summing up (A1) and (A3), we find that the integrand of the surface integral in (1) containing f_{24} (4) does not contain the derivatives normal to the surface S, i.e.,

$$-\frac{\sqrt{g}f_{24}}{K_{22}+K_{24}}=\sqrt{g}J_S+n_3^2\partial_3\sqrt{g_{11}g_{22}}+n_3\partial_s\left[n_s\left[\frac{g}{g_{ss}}\right]^{1/2}\right] . \tag{A5}$$

But at the same time, the normal derivative ∂_3n_3 enters the K_{13} term as is seen from (A1). We shall show now that if the integrand contains only derivatives along the tangential directions, then integration over the surface results in the variation δF_{24} of the integral $F_{24}=\int dS\, f_{24}$ to be independent of the director derivative variations $\delta\partial_i n_k$. Let us find the variation of the functional F_{24} under the condition $\mathbf{n}^2=1$,

$$\delta F_{24}=\int dS\left\{\frac{\partial f_{24}}{\partial n_k}\delta n_k+\frac{\partial f_{24}}{\partial(\partial_s n_k)}\delta(\partial_s n_k)+\lambda_S n_k\delta n_k\right\} , \tag{A6}$$

where $\lambda_S=\lambda_S(x_1,x_2)$ is the Lagrange (surface) factor, $dS=\sqrt{g_{11}g_{22}}dx_1dx_2$. Taking into account the equality $\delta(\partial_s n_k)=\partial_s\delta n_k$ and performing integration by parts in (A6), we find that

$$\delta F_{24}=\int dS\left\{\frac{\partial f_{24}}{\partial n_k}-\frac{1}{\sqrt{g_{11}g_{22}}}\partial_s\left[\sqrt{g_{11}g_{22}}\frac{\partial f_{24}}{\partial(\partial_s n_k)}\right]+\lambda_S n_k\right\}\delta n_k \equiv\int dS\frac{\delta f_{24}}{\delta n_k}\delta n_k . \tag{A7}$$

This is valid if the surface S is smooth. If, however, it consists of smooth parts S_μ with the boundary contours l_μ, then

$$\delta F_{24}=\sum_\mu \int \frac{\delta f_{24}}{\delta n_k}\delta n_k dS_\mu + \sum_\mu \oint dl_\mu \left\{\cos\alpha_s \frac{\partial f_{24}}{\partial_s n_k}+\frac{\partial f_{Ed}}{\partial n_k}\right\}\delta n_k , \tag{A8}$$

where $\oint dl_\mu$ is the integral over l_μ and α_S is the angle between external normal to l_μ and the coordinate line x_s. By analogy to the anchoring surface energy $\int f_A(\mathbf{n})dS$, we introduced here the anchoring edge energy $F_{Ed}=\sum_\mu \oint dl_\mu f_{Ed}(\mathbf{n})$. In what follows we assume S to be a smooth surface and equality (A7) to be satisfied.

Thus, the variation F_{24} is a functional only on δn_k similarly to δF_F and δF_A. Therefore, the total variation under the condition $\mathbf{n}^2=1$ is given by

$$\delta F=\int dV\left\{\frac{\partial f_F}{\partial n_k}-\frac{1}{\sqrt{g}}\partial_m\left[\sqrt{g}\frac{\partial f_F}{\partial(\partial_m n_k)}\right]+\lambda_V n_k\right\}\delta n_k + \int dS\left\{\frac{\partial f_F}{\partial(\partial_3 n_k)}+\frac{\partial f_A}{\partial n_k}+\frac{\delta f_{24}}{\delta n_k}+\lambda_S n_k\right\}\delta n_k , \tag{A9}$$

where $\lambda_V(\mathbf{x})$ is the volume Lagrange factor. Equating to zero each of the expressions within the curly brackets, we obtain the Euler-Lagrange equations (A10) and the boundary conditions (A11) to be

$$\frac{\partial f_F}{\partial n_k}-\frac{1}{\sqrt{g}}\partial_m\left[\sqrt{g}\frac{\partial f_F}{\partial(\partial_m n_k)}\right]+\lambda_V n_k=0 , \quad \mathbf{x}\in V , \tag{A10}$$

$$\frac{\partial f_F}{\partial(\partial_3 n_k)}+\frac{\partial f_A}{\partial n_k}+\frac{\partial f_{24}}{\partial n_k}-\frac{1}{\sqrt{g_S}}\partial_s\left[\sqrt{g_S}\frac{\partial f_{24}}{\partial(\partial_s n_k)}\right]+\lambda_S n_k=0 , \quad x_3=S_0 , \tag{A11}$$

where $g_S=g_{11}g_{22}$. Thus, the minimum of the total functional F containing the K_{24} term occurs on the family of functions which satisfy the Euler-Lagrange equations (A10). The K_{24} term does not contribute in these equations similarly to any term of divergence form, but it changes the boundary conditions (A11). It is clear that, in contrast to the tangent derivatives $\partial_s\mathbf{n}$, the normal ones, $\partial_3\mathbf{n}$, cannot be eliminated by means of the integration over $dx_1 dx_2$, and the variation of the functional F_{13} depends on their variation $\delta\partial_3\mathbf{n}$. These can be infinite and can lead to unboundedness of the F_{13} variation from below. This possibility is confirmed in Sec. II.

The geometrical structure of the surfacelike terms suggests that it is convenient to rearrange their contribution in a way which geometrically is even more natural than separation into the K_{13} and K_{24} terms; namely, let us separate the normal and tangential derivatives in the total contribution $f_{13}+f_{24}$. From (A1)–(A5) one can easily obtain such a representation to be

$$f_{13}+f_{24}=f_{S,\parallel}+f_{S,\perp} , \tag{A12}$$

$$f_{S,\parallel}=-(K_{22}+K_{24})J_S+\frac{K_{13}-K_{22}-K_{24}}{\sqrt{g}}\left[n_3^2\partial_3\sqrt{g_S}+n_3\partial_s(n_s\sqrt{g/g_{ss}})\right] , \tag{A13}$$

$$f_{s,\perp}=K_{13}\frac{n_3\partial_3 n_3}{\sqrt{g_{33}}} . \tag{A14}$$

Thus, the surface density $f_{S,\parallel}$, containing the tangential-to-S director derivatives, will appear in formulas (A6)–(A9) and (A11) instead of f_{24} if both K_{13} and K_{24} contributions are taken into account. The remaining part, $f_{S,\perp}$, which contains the normal-to-S director derivative, and which is, in fact, the most essential part of the K_{13} term, is incorporated into the variational procedure for the one-dimensional case in Sec. VI. Note that the minimizing procedure proposed in Sec. VI [solving the Euler-Lagrange equations and subsequently minimizing the functional $P(c)$ with respect to arbitrariness c] is always applicable. However, a generalization of the explicit boundary conditions (25) to the three-dimensional case requires more detailed information about the arbitrariness $c(\mathbf{x})$.

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[30] G. Barbero and A. Strigazzi, J. Phys. (Paris) Lett. **45**, 857 (1984).
[31] Though both Eqs. (25) and Hinov's approach are based upon the solution of the ELE, the boundary condition obtained in Ref. [9] crucially differs from (25). In accordance with the very sense of minimization with respect to the parameters θ_1 and θ_2, the differentiation in the last terms of (25) is performed with respect to these parameters. This implies that θ' is a known function of θ_1 and θ_2, i.e., $\theta'=\theta'(z=\text{const},\theta_1,\theta_2)$, so that $d\theta'/d\theta_1 = d\theta'(\theta_1,\theta_2)/d\theta_1$. Instead of $d\theta'(z=-d/2)/d\theta_1$ Hinov's boundary condition [9] contains $[(d^2\theta/dz^2)(d\theta/dz)^{-1}]$ $(z=-d/2)$. The last expression can be written as $d\theta'/d\theta$ only if θ and θ' are regarded as functions of z rather than of θ_1 and θ_2. To illustrate the difference, let us assume θ to be the solution of the ELE in the one-constant approximation: $\theta(z)=[(\theta_2-\theta_1)/2d]z + (\theta_1+\theta_2)/2$. Then $\theta'(\theta_1,\theta_2)=(\theta_2-\theta_1)/2d$ and $d\theta'(\theta_1,\theta_2)/d\theta_1=-1/2d$, whereas $\theta''\theta'^{-1}=0$.