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Perturbative approach to the structure of a planar interface in the Landau–de Gennes model

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The structure of nearly static planar interfaces is studied within the framework of the Landau–de Gennes model with the dynamics governed by the time-dependent Ginzburg-Landau equation. To account for the full elastic anisotropy the free energy expansion is extended to include a third order gradient term. The solutions corresponding to the in-plane or homeotropic director alignment at the interface are sought. For this purpose a consistent perturbative scheme is constructed which enables one to calculate successive corrections to the velocity and the order parameter of the interface. The implications of the solutions are discussed. The elastic anisotropy introduces asymmetry into the order parameter and free energy profiles, even for the high symmetry homeotropic configuration. The velocity of the interface with the homeotropic or in-plane alignment is enhanced or reduced, respectively. There is no reorientation of the optical axis in the boundary layer. For the class of nematogens with approximate splay-bend degeneracy the temperature dependence of the interface velocity is weakly affected by the remaining twist anisotropy.

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I. INTRODUCTION

In a system undergoing a first order phase transition, instability with respect to fluctuations that are large in amplitude but small in spatial extent occurs as the temperature is lowered. In consequence the system separates into two phases with an interface between them. The exploration of the dynamics of such interfaces both theoretically and experimentally are to yield considerable insight into the phase transformation process, see, e.g., [1] for a recent review. From the theoretical point of view, especially appealing and challenging is the fact that the problem is intrinsically nonlinear. The present paper addresses the problem of the propagation and structure of a planar interface between the nematic (N) and isotropic liquid (I) phases within a coarse-grained description provided by the Landau–de Gennes theory.

The problem of the properties of interfaces in nematic liquid crystals was addressed as soon as an appropriate theory of the phase transition in those media—the Landau–de Gennes theory—had been formulated [2]. In [3], by means of a variational calculation and under the assumption of uniaxiality of the medium at all points in the flat transition layer it was shown that the minimum of the free energy occurs either for the parallel or perpendicular orientation of the optical axis with respect to that layer depending on the sign of the second elastic constant L_2 introducing an anisotropic second order gradient term into the model. It was, however, stressed that a complete elucidation of the problem would demand much more elaborate calculations. In response to that, the structure of a planar N/I phase boundary was investigated in [4] within the framework of the same formalism. By analyzing the free energy contributions it was argued that the structure of the boundary depends significantly on the orientation of the optical axis with respect to the plane of that boundary. It was qualitatively shown that for the homeotropic director alignment the phase boundary possesses the structure of a uniaxial crystal, whereas the in-plane alignment leads to the occurrence of weak biaxiality inside the boundary layer. It was also pointed out that in the interfacial region the reorientation of the optical axis should occur. However, no analytical solutions, even approximate, to justify the latter statement have been given. The above conjectures were followed by the numerical studies of the problem, where two main approaches have been taken. First, the properties of the planar N/I interface were investigated on the statistical-molecular level [5,6], which yielded the density and order parameter profiles together with the free energy distribution in the cases of the homeotropic and in-plane alignment. The calculations confirmed the occurrence of biaxiality in the latter case, and the lack of it in the former one. The starting point of the other approach [7] was the dynamical tensor model offered by the time-dependent Ginzburg-Landau (TDGL) equation. The numerical solutions revealed an array of effects due to the elastic anisotropy, the prominent one being a massive reduction of the interface velocity as compared to the value obtained with the de Gennes variational solution. However, in [7] only second order terms in the order parameter were retained, which is known to fail to account for the experimentally found difference between the splay and bend elastic constants.

The present paper joins in the above works. Its main purpose is to account for the full elastic anisotropy of the nematic liquid crystal, which is obtained by extending the elastic free energy density to include a third order term, i.e.,

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$$\mathcal{F}_e = \frac{1}{2}L_1 \partial_i Q_{jk} \partial_i Q_{jk} + \frac{1}{2}L_2 \partial_i Q_{ik} \partial_j Q_{jk} + \frac{1}{2}L_3 Q_{ij} \partial_i Q_{kl} \partial_j Q_{kl}, \tag{1}$$

where $\hat{Q}=[Q_{ij}]$ $(i,j=1,2,3)$ is the symmetric, traceless, second-rank tensor order parameter of the nematic liquid crystal, L_1, L_2, L_3 are the elastic coefficients, and for repeated indices the Einstein summation convention is assumed. The addition of the third order term is not a unique procedure as in a generic case six linearly independent third order invariants can be constructed [8]. However, the particular term we include was reported to be sufficient to reproduce correctly the temperature dependence of the Oseen-Frank elastic constants for a typical nematogen PAA (*p*-azoxyanisole) [9]. Moreover, the best-fit values for the elastic constants were found ($L_1=10.5$, $L_2=13.9$, $L_3=20$ in 10^{-12} N), which will serve as a natural quantitative basis for our calculations. For stability reasons a fourth order term should also be included, but the corrections from such a term are expected to be relatively smaller, so we believe that the truncated model will reproduce all the essential effects.

The realistic description of the dynamics of the N/I interface would require solving a system of equations of the full nematodynamics [10,11]. This represents obviously a formidable task, unless some simplifying assumptions are made. There are two main assumptions which we make here. First, the dynamics is assumed as in [7] to be governed by the TDGL equation. The TDGL theory is known to have found wide application ranging from the kinetic theory of phase transitions [12,13], the phase-field models of solidification [14] to the propagation of signals in electric circuits [15], and the theoretical population biology [16]. That simplification is justified as far as the viscous force of the fluid is so weak as compared with the elastic force of the liquid crystal that the fluid flow preserves the orientation profile. A dimensionless quantity measuring the relative magnitude of these effects is given by the Ericksen number

$$Er = \frac{\eta l V}{K}, \tag{2}$$

where, generally, η, l, V, and K denote a characteristic viscosity, length scale, velocity, and elasticity coefficient of the system, respectively. The requirement that $Er \ll 1$, and assuming the typical values for the coefficients in Eq. (2) ($\eta=0.1$ Pa s, $K=10^{-11}$ N, $l=10^{-8}$ m—the coherence length) leads to the constraint on the velocity values, i.e., $V \ll 1$ cm/s, for which such a simplified picture holds plausible. The second assumption is related to the fact that any transition of the first kind is accompanied by the effect of emission or absorption of latent heat at the interface. The presence of this moving heat source or sink brings into the problem the requirement of conservation of energy. The proper course would be to treat the temperature field $T(\vec{r},t)$ simultaneously as a secondary order parameter. However, it is assumed here that in the course of the phase transformation the latent heat is conducted infinitely fast to the external environment. A serious breakdown of the isothermal condition may be avoided by working with a small rate of decrease of the total free energy. Then one can hope that the temperature buildup due to the latent heat will be small. It is clear that such a situation corresponds to small propagation rates of the interface or equivalently to a limited degree of supercooling or superheating. Although the simplified model remains reliable for slowly moving or static interfaces, the results covering the full N/I-phase coexistence region provide a good reference point for the studies of interfaces within the full nematodynamics.

Our purpose is accomplished by an independent analytical method. The solutions of the TDGL equation corresponding to the moving flat interface are obtained within a consistent perturbative scheme. The fact that the first order corrections to $\hat{Q}$ are found to be two orders of magnitude smaller than the zeroth order contribution provides a good justification of that approach. A natural starting point for such a scheme is an exactly soluble model. For the in-plane configuration it is the fully isotropic case of $L_2=L_3=0$, whereas for the homeotropic configuration an exact solution is found within the two-constant approximation, where only $L_3=0$. Corrections to the order parameter are obtained order by order as solutions of ordinary, linear differential equations, while corrections to the velocity of the interface follow from certain integrability conditions, which are due to the existence of the translational zero mode. These types of integrability conditions is well-known in statistical physics [17]. That technique, though not new [18], is extended here to the nontrivial case of the tensor phase field and is demonstrated to be a potent tool providing explicit insight into the structure of the N/I interface. An important and convenient aspect of the presented scheme is that it encompasses a generic case of a moving interface, that is, when the nematic and isotropic liquid phase are out of equilibrium, one being stable and the other metastable.

With the corresponding solutions a number of physical effects have been revealed. The elastic anisotropy introduces asymmetry across the interfacial region of both configurations. Relaxing the splay-bend degeneracy for the in-plane alignment enhances the biaxiality mode preserving its profile with a pronounced maximum on the I-phase side. Let us also add that the perturbative scheme provides the biaxiality degree in the easily reproducible form of one-dimensional integrals. Similarly, the symmetry restoring feature reported in Ref. [7] is enhanced, however, it is clearly demonstrated that unlike it was suggested the negative order parameter region is an intermediate one separating two regions in which the orientations of the optical axis are perpendicular to each other. Furthermore, it is found for both configurations that no reorientation of the optical axis takes place, contrary to what was conjectured in [4]. Exclusively due to the energetical nonequivalence of splay and bend deformations, a region of lowered tension appears on the N-phase side for the in-plane alignment. That feature is absent in the homeotropic configuration. The decrease (increase) of the free energy of the interface for the in-plane (homeotropic) configuration implies the decrease (increase) of elasticity with respect to the isotropic approximation. This in turn accounts for the steeper-sloping (more-gentle-sloping) ordering and free-energy-density profiles. The substantial decrease (increase) of the interface velocity relative to the value obtained by the isotropic approximation for the in-plane (homeotropic) alignment is also directly attributable to that reduction (enhancement) of elasticity. Interestingly, for nematogens with the splay and bend elastic constants nearly equal, when one can neglect the correction due to the L_3-term, the first order velocity correction does not depend on temperature (in-plane alignment), or vanishes (homeotropic alignment). The calculation of the second order correction leads to the conclusion that for this class of nematogens the elastic anisotropy does not affect considerably the temperature dependence of the interface velocity.

Finally, the paper opens the way for investigations of the evolution of curved interfaces in nematic liquid-crystals. A carefully designed expansion in curvatures [19], for which the knowledge of the solution corresponding to the flat geometry of the interface is the only prerequisite, could provide new insights into the dynamics of the bubbles of the stable phase nucleating in the environment of the unstable one.

The paper is organized as follows. In Sec. II we recall the main features of the Landau–de Gennes model, remark on the symmetries of the problem, and go on to discuss the boundary conditions and the pertinent evolution equation and its implications. In Sec. III the solution corresponding to the interface with the in-plane director alignment is constructed. The perturbative scheme is presented and the first order corrections to the order parameter field and the free energy are calculated. Section IV lists concisely the solution obtained for the interface with the homeotropic director alignment. In Sec. V we collect and discuss the features revealed by the solutions. And finally, Sec. VI concludes the paper with some additional remarks.

II. PRELIMINARIES

As already mentioned the order parameter for the nematic liquid crystal in the Landau–de Gennes model has the form of a symmetric traceless real tensor $\hat{Q}$. The corresponding free energy density comprises two components $\mathcal{F}=\mathcal{F}_b+\mathcal{F}_e$. The bulk contribution is assumed in the standard form

$$\mathcal{F}_b = \frac{1}{2}\mathcal{A}\,\mathrm{Tr}\,\hat{Q}^2 - \frac{1}{3}\mathcal{B}\,\mathrm{Tr}\,\hat{Q}^3 + \frac{1}{4}\mathcal{C}(\mathrm{Tr}\,\hat{Q}^2)^2, \tag{3}$$

where the coefficient $\mathcal{A}$ is assumed to depend linearly on temperature, that is $\mathcal{A}=a(T-T^*)$. Constants $a,\mathcal{B},\mathcal{C},L_1,L_2$ characterize the liquid crystalline material and we assume them to be temperature-independent, see, e.g., [20]. For the standard stability reasons constants a and $\mathcal{C}$ are taken to be positive. Furthermore, for most nematogenic compounds [11,20], the ground state proved to be that of a uniaxial prolate ordering, which implies a positive value of constant $\mathcal{B}$ as well. By minimizing $\mathcal{F}_b$ it is shown that for a temperature in the interval $(T^*,T^\dagger)$, where $T^\dagger=T^*+\mathcal{B}^2/24a\mathcal{C}$, there are two local minima. For $T\in(T^*,T_{NI})$, where $T_{NI}=T^*+\mathcal{B}^2/27a\mathcal{C}$, one of the minima corresponds to the stable uniaxial nematic phase, whereas the other to the metastable state of the supercooled isotropic phase. Increasing the temperature above the clearing point T_{NI} renders the isotropic phase stable, whereas the nematic phase becomes metastable and its superheating occurs. The ground state of the free energy is obviously degenerate and the corresponding order parameter values can be obtained as $\hat{Q}_g=\mathcal{O}\hat{Q}_0(T)\mathcal{O}^{\mathrm{T}}$, where $\mathcal{O}\in O(3)$ and $\hat{Q}_0(T)=S_0(T)\mathrm{diag}[1,-1/2,-1/2]$. The eigenvector corresponding to the nondegenerate eigenvalue of $\hat{Q}_0(T)$ defines the direction of the average orientation of the molecules, i.e., the optical axis or the director $\vec{n}$. The temperature-dependent function S_0 is the so-called scalar order parameter, giving the degree of the orientational order of nematogenic molecules. Straightforward calculation yields

$$S_0(\tau)=\begin{cases} 0 & \text{for } 8/9<\tau<1, \\ \dfrac{\mathcal{B}}{6\mathcal{C}}[1+\sqrt{1-\tau}] & \text{for } 0<\tau<8/9. \end{cases} \tag{4}$$

Here, a useful dimensionless measure of temperature has been introduced $\tau=(T-T^*)/(T^\dagger-T^*)$. At $\tau=8/9$ $(T=T_{NI})$ the order parameter S_0 experiences a jump of magnitude $\frac{2\mathcal{B}}{9\mathcal{C}}$.

The physical importance of the Landau–de Gennes model bears upon the fact that it enables one to describe not only the spatially uniform ground states but also states belonging to a much wider class where $\hat{Q}$ is space and time dependent, $\hat{Q}=\hat{Q}(\vec{r},t)$. The energetic penalty related to the nonuniformities of the orientation field is taken into account by the elastic term of the free energy density $\mathcal{F}_e$. As discussed in Sec. I, in the present study we go beyond the second order in $\hat{Q}$ and include a third order term, cf. Eq. (1). In the two-constant approximation the requirement that a spatially uniform state be stable against local distortions sets restrictions on the values of the elastic constants, i.e., $L_1>0$ and $L_2>-3/5L_1$ [3,21]. The extension lifts the degeneracy of the Oseen-Frank splay and bend elastic constants. In London's approximation, i.e., by restricting the configurations to the vacuum manifold, one can recast the elastic free energy density into the form of the Oseen-Zöcher-Frank formalism [11,22] and find the following relations between the L-constants and the Oseen-Frank splay, twist, and bend elastic constants K_{11}, K_{22}, K_{33}, respectively,

$$K_{11}=\frac{9}{4}S_0^2(2L_1+L_2-S_0L_3), \quad K_{22}=\frac{9}{4}S_0^2(2L_1-S_0L_3),$$

$$K_{33}=\frac{9}{4}S_0^2(2L_1+L_2+2S_0L_3).$$

From the requirement that these elastic constants be positive one obtains the following restrictions on the values of L_3: $-(2L_1+L_2)/2<L_3S_0<\min(2L_1,2L_1+L_2)$. It shows that like L_2 the negative values of the elastic constant L_3 are not excluded. Let us stress that the above condition is rather tentative as it was derived in the specific case where the spatial changes of the scalar order parameter are negligible and the higher order terms were absent.

Previous studies [3,4,7] have pointed out that the interface with the in-plane or homeotropic alignment of the director correspond to the free energy extrema. They are also known to be singled out by the symmetries underlying the system [23]. The former configuration is characterized by the symmetry group $H_{NI}^{(1)}=t_{(2)}\times C_{2v}$, whereas the latter by $H_{NI}^{(2)}=t_{(2)}\times C_{\infty v}$, where $t_{(2)}$ denotes the group of translations along the directions parallel to the interface plane, and where the rotation axis in groups C_{2v} and $C_{\infty v}$ is perpendicular to the interface plane. They define the number of independent components of the order parameter for the two types of ordering in the boundary layer. The in-plane configuration involves three degrees of freedom: in addition to the scalar order parameter, there are biaxiality and rotations about the axis perpendicular to the interface plane. The homeotropic symmetry $H_{NI}^{(2)}$ allows for one degree only, i.e., the scalar order parameter.

It is clear that for the solution to be unique in the given symmetry class one has to fix the boundary conditions. We consider here the case of infinitely extended interfaces, so there are no boundaries on either side of the interfacial region. Let us next assume that the isotropic phase is always to be found for $x^3\to-\infty$. Since the order parameter of the isotropic phase vanishes the first boundary condition reads $\hat{Q}^{(i)}(x^3\to-\infty)=\mathbf{0}$, where index $i=1,2$ refers to the two configurations of the interface discussed above, and $\mathbf{0}$ denotes the zero matrix. Note that the above condition does not impose any restrictions on the orientation of the optical axis which is of no physical significance on that side of the interface. By contrast, on the N-phase side, where $\hat{Q}^{(i)}\neq\mathbf{0}$, the corresponding boundary condition is to fix the orientation of the optical axis. In general, it is defined by an orthogonal matrix whose components depend on the transverse coordinates x^1, x^2. We confine ourselves to the class of the boundary conditions homogeneous in the x^1x^2-plane. Then, the flat interface is the local minimum of the free energy. Furthermore, in both cases we assume that the orientation of the director far away from the boundary layer ($x^3\to+\infty$) is consistent with that implied by the corresponding symmetry classes. That prevents the occurrence of boundary-induced reorientation of the optical axis which would blur the anisotropy-induced effects.

With the assumptions discussed in Sec. I the pertinent evolution equation reduces to the form of the TDGL type [10]

$$\eta\frac{\partial\hat{Q}}{\partial t}=-\frac{\delta F}{\delta\hat{Q}}. \tag{5}$$

The positive frictional coefficient η accounts for the dissipative effects accompanying the reorientation processes in the liquid crystalline medium, and is related to the rotational viscosity γ_1 [10,11]. F denotes the total free energy of the system given by the $\hat{Q}$-dependent functional

$$F[\hat{Q}(\vec{r},t)]=\int d^3\vec{r}\mathcal{F}. \tag{6}$$

That type of evolution equation encodes the simple empirical fact that a physical system, when displaced away from the equilibrium state, will relax back to it. The functional derivative on the right-hand side (rhs) of Eq. (5) represents the thermodynamic force that drives the system towards equilibrium.

The underlying model is translationally invariant, as the free energy density $\mathcal{F}$ does not explicitly depend on the spatial coordinates x^i $(i=1,2,3)$. The Noether theorem implies then the following identity [24]:

$$\frac{\mathcal{D}\Sigma_{kl}}{\mathcal{D}x^k}-\frac{\delta F}{\delta Q_{ij}}\frac{\partial Q_{ij}}{\partial x^l}=0, \tag{7}$$

where

$$\Sigma_{kl}=\mathcal{F}\delta_{kl}-\frac{\partial\mathcal{F}}{\partial(\partial_k Q_{ij})}\partial_l Q_{ij}, \tag{8}$$

and $\mathcal{D}/\mathcal{D}x^k$ denotes the so-called substantial derivative with respect to x^k. $\hat{\Sigma}$ is a generalization of the Ericksen strain tensor pertinent to the Landau–de Gennes model [11,25]. Equations (5) and (7) imply

$$\frac{\mathcal{D}\Sigma_{kl}}{\mathcal{D}x^k}+\eta\,\mathrm{Tr}\left(\frac{\partial\hat{Q}}{\partial t}\frac{\partial\hat{Q}}{\partial x^l}\right)=0, \tag{9}$$

which can be interpreted as the local nematodynamical equilibrium equation. Let us integrate both sides of Eq. (9) over the region closed in the long cylinder whose symmetry axis coincides with the x^3-axis and the bases lie in the planes parallel to the x^1x^2-plane. In the limit of an infinite length of that cylindrical region Eq. (9) yields

$$\eta\int_{-\infty}^{+\infty}dx^3\,\mathrm{Tr}\left(\frac{\partial\hat{Q}}{\partial t}\frac{\partial\hat{Q}}{\partial x^3}\right)=\mathcal{F}_b(\hat{Q}_I)-\mathcal{F}_b(\hat{Q}_N), \tag{10}$$

where $\hat{Q}_I$ and $\hat{Q}_N$ are the values of the order parameter corresponding to the isotropic liquid and nematic phase, respectively. It is apparent that the rhs of Eq. (10) is, in general, nonzero and independent of t. So must, therefore, be the left-hand side (lhs) of Eq. (10). The simplest assumption consistent with Eq. (10) is that the order parameter is a function of the combined variable ξ, where $\xi=x^3-\mathcal{V}t$. Then, for the velocity of a planar interface Eq. (10) yields

$$\mathcal{V}=\frac{\mathcal{F}_b(\hat{Q}_N)}{\eta\int_{-\infty}^{+\infty}d\xi\,\mathrm{Tr}(\partial_\xi\hat{Q})^2}, \tag{11}$$

where we used the fact that $\mathcal{F}_b(\hat{Q}_I)=0$. It has been thus shown that in the given model there exist solutions corresponding to planar interfaces with a constant propagation rate.

In conclusion, the interface with the in-plane and homeotropic alignment will be the subject of the following considerations. It is noteworthy that for the in-plane configuration the symmetry itself indicates that biaxiality and the director reorientation may appear in the boundary layer. Whether they do or not depends crucially on the pertinent evolution equation. To elucidate that question a perturbative scheme will be developed.

III. THE INTERFACE STRUCTURE FOR THE IN-PLANE ALIGNMENT

To arrive at the explicit form of the evolution equation (5) one has to take into account the symmetries of the order parameter. This is done by adding to the free energy density a term of the form $\mathrm{Tr}(\hat{\Lambda}\hat{Q})$ with the generalized Lagrange multiplier $\Lambda_{ij}=\lambda_0\delta_{ij}-\epsilon_{ijk}\lambda_k$, where δ_{ij} is the Kronecker delta and ϵ_{ijk} the totally antisymmetric Levi-Civita tensor. The standard procedure yields the following evolution equation:

$$\begin{aligned}\eta\frac{\partial Q_{ij}}{\partial t} = {} & \left(L_1+\frac{1}{2}L_2\right)\partial_k\partial_k Q_{ij} - \mathcal{A}Q_{ij} + \mathcal{B}\hat{Q}^2_{ij} - \mathcal{C}\,\mathrm{Tr}\,\hat{Q}^2 Q_{ij} \\ & - \frac{1}{3}\mathcal{B}\,\mathrm{Tr}\,\hat{Q}^2\delta_{ij} - \frac{1}{6}L_2[2(\partial_k\partial_l Q_{kl})\delta_{ij} - 3(\partial_i\partial_k Q_{kj} \\ & + \partial_j\partial_k Q_{ki}) + 3\partial_k\partial_k Q_{ij}] - \frac{1}{6}L_3[3\partial_i Q_{kl}\partial_j Q_{kl} \\ & - 6\partial_k(Q_{kl}\partial_l Q_{ij}) - (\partial_m Q_{kl}\partial_m Q_{kl})\delta_{ij}], \end{aligned} \tag{12}$$

where some reshuffling of terms was done which we will refer to shortly. One can easily check that a uniaxial ansatz fails to satisfy Eq. (12), unless elastic constants $L_2=L_3=0$. Thus the evolution equation enforces biaxiality for the interface with the in-plane alignment. Yet, an exact analytical solution for the biaxial ansatz is not known. The analytical solution in the isotropic approximation, however, is well-known [4,13]. In what follows we show that the structure of the order parameter might be found within the framework of a perturbative expansion with the isotropic approximation serving as its zeroth order. The objective of the present section is to report the construction of such a perturbative scheme as well as to discuss its plausibility.

A. The construction of the perturbative scheme

The reshuffling of terms in Eq. (12) is equivalent to dividing the free energy density into two parts, i.e., $\mathcal{F}=\mathcal{F}_0+\delta\mathcal{F}$, where the unperturbed part is given by the formula

$$\begin{aligned}\mathcal{F}_0 = {} & \frac{1}{2}\left(L_1+\frac{1}{2}L_2\right)\partial_k Q_{ij}\partial_k Q_{ij} + \frac{1}{2}\mathcal{A}\,\mathrm{Tr}\,\hat{Q}^2 - \frac{1}{3}\mathcal{B}\,\mathrm{Tr}\,\hat{Q}^3 \\ & + \frac{1}{4}\mathcal{C}(\mathrm{Tr}\,\hat{Q}^2)^2, \end{aligned} \tag{13}$$

and the perturbation term has the form

$$\delta\mathcal{F} = \frac{1}{4}L_2(2\partial_i Q_{ik}\partial_j Q_{jk} - \partial_k Q_{ij}\partial_k Q_{ij}) + \frac{1}{2}L_3 Q_{ij}\partial_i Q_{kl}\partial_j Q_{kl}. \tag{14}$$

The unperturbed model has been defined to correspond to the so-called one-constant approximation in the Oseen-Zöcher-Frank formalism with $K_{11}=K_{22}=K_{33}=\frac{9}{4}S_0^2(2L_1+L_2)$. We define two dimensionless expansion parameters of the perturbative series

$$\varepsilon_2 = \frac{2L_2}{2L_1+L_2}, \quad \varepsilon_3 = \frac{L_3 S_0}{2L_1+L_2}. \tag{15}$$

Note that ε_3 is temperature-dependent through S_0. Adopting the data from [9] for PAA, we arrive at the following estimates for the expansion parameter $\varepsilon_2\approx 0.8$ and $\varepsilon_3\approx 0.57S_0$. The fact that these values are comparable to unity does not mean that perturbative calculations are out of place here, as one should remember that what is relevant is not the value of the expansion parameter itself but the order of magnitude of a full correction.

It was shown in Sec. II that the evolution equation (5) allows for the existence of steady-state solutions, i.e., such that $\hat{Q}=\hat{Q}(\xi=x^3-\mathcal{V}_{\parallel}t)$ where the subscript $\parallel$ is to refer to the case of the parallel in-plane alignment. Equation (12) reduces then to an ordinary differential equation where only the derivatives with respect to ξ are present. It is convenient to use a rescaled order parameter $\hat{q}$ defined by the formula $\hat{Q}=S_0(\tau)\hat{q}$, and to replace the variables ξ and $\mathcal{V}_{\parallel}$ by their dimensionless counterparts s and υ, respectively. They are defined by the following chain of equations:

$$\xi = \xi_{\parallel}(\alpha,\varepsilon_2)s, \tag{16}$$

$$\xi_{\parallel}(\alpha,\varepsilon_2) = \sqrt{\frac{2}{2-\varepsilon_2}}\xi_0(\alpha), \quad \xi_0(\alpha) = \frac{4\sqrt{3\mathcal{C}L_1}}{\mathcal{B}}(1+\alpha),$$

$$\mathcal{V}_{\parallel}(\alpha,\varepsilon_2) = \mathcal{V}_0(\alpha)\sqrt{\frac{2}{2-\varepsilon_2}}\upsilon, \quad \mathcal{V}_0(\alpha) = \frac{\mathcal{B}}{2\eta}\sqrt{\frac{L_1}{3\mathcal{C}}}\frac{2\alpha-1}{1+\alpha}, \tag{17}$$

$$\alpha = \frac{2\mathcal{A}}{3\mathcal{C}S_0^2(\tau)},$$

where α is another convenient dimensionless temperature parametrization. Like τ it increases monotonically from 0 to 1 while T varies from T^* to $T^\dagger$, but the clearing point T_{NI} corresponds now to $\alpha=1/2$. It can be readily shown that $\alpha=(1-\sqrt{1-\tau})/(1+\sqrt{1-\tau})$. The above choice of the dimensionless variables s and α ensures enhanced simplicity and clarity of the ensuing formulas. Let us also note that the factorization of $(2\alpha-1)$ in the definition of υ in Eq. (17) is a nontrivial implication of Eq. (11). In the new variables the evolution equation reads

$$\begin{aligned} & \frac{1}{2}\frac{d^2q_{ij}}{ds^2} + (2\alpha-1)\upsilon\frac{dq_{ij}}{ds} - 4\alpha q_{ij} + 8(1+\alpha)\hat{q}^2_{ij} - \frac{8}{3}\mathrm{Tr}\,\hat{q}^2 q_{ij} \\ & \quad - \frac{8}{3}(1+\alpha)\mathrm{Tr}\,\hat{q}^2\delta_{ij} - \frac{1}{6}\varepsilon_2\left[\frac{d^2q_{33}}{ds^2}\delta_{ij} - \frac{3}{2}\left(\delta_{3i}\frac{d^2q_{3j}}{ds^2}\right.\right. \\ & \quad \left.\left. + \delta_{3j}\frac{d^2q_{3i}}{ds^2}\right) + \frac{3}{2}\frac{d^2q_{ij}}{ds^2}\right] - \frac{1}{6}\varepsilon_3\left[3\frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{i3}\delta_{j3}\right. \\ & \quad \left. - 6\frac{d}{ds}\left(q_{33}\frac{dq_{ij}}{ds}\right) - \frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{ij}\right] = 0. \end{aligned} \tag{18}$$

The construction of the perturbative scheme goes along similar lines like those reported in [18]. What is nontrivial in the present problem is the tensorial structure of the order parameter, while [18] involved a single real-valued scalar order parameter. We postulate the following perturbative expansions for the order parameter and the velocity of the interface:

$$\hat{q} = \sum_{\mu,\nu=0}^{\infty} \varepsilon_2^{\mu}\varepsilon_3^{\nu} q_{(\mu,\nu)}, \quad v = \sum_{\mu,\nu=0}^{\infty} \varepsilon_2^{\mu}\varepsilon_3^{\nu} v_{(\mu,\nu)}. \tag{19}$$

Let us stress that in Eq. (18) as well as in expansion (19) the independent variable is just s and not x^3 or t hidden inside it. Therefore when solving Eq. (18) we do not expand s in ε_2, contrary to what formulas in Eqs. (16) and (17) might suggest. Only after $\hat{q}$ and v are determined do we substitute $\xi/\xi_{\parallel}(\alpha,\varepsilon_2)$ for s in order to relate the solution of Eq. (18) to the interface solution of the original Eq. (12). Inserting expansions given in Eq. (19) into Eq. (18) and equating to zero terms proportional to the successive products $\varepsilon_2^{\mu}\varepsilon_3^{\nu}$ on the lhs of Eq. (18) we arrive at an infinite chain of equations for the consecutive terms $\hat{q}_{(\mu,\nu)}$ $(\mu \geqslant 0, \nu \geqslant 0)$ of the order parameter expansion. The zeroth order contribution must obey the following nonlinear equation:

$$\frac{1}{2}\frac{d^2\hat{q}_0}{ds^2} + (2\alpha-1)v_0\frac{d\hat{q}_0}{ds} - 4\alpha\hat{q}_0 + 8(1+\alpha)\hat{q}_0^2 - \frac{8}{3}(\mathrm{Tr}\,\hat{q}_0^2)\hat{q}_0 - \frac{8}{3}(1+\alpha)(\mathrm{Tr}\,\hat{q}_0^2)I = 0, \tag{20}$$

while the shape of higher order corrections is governed by the linear equations of the form

$$\hat{\mathcal{L}}(\hat{q}_0)[\hat{q}_{(\mu,\nu)}] = \hat{\mathcal{N}}_{(\mu,\nu)}, \tag{21}$$

where we introduced a simplifying notation $\hat{q}_0 \equiv \hat{q}_{(0,0)}$, and the operator $\mathcal{L}(\hat{q}_0)$ together with a formal recipe to obtain the inhomogeneous terms are given in Appendix A.

As already mentioned the underlying model is translationally invariant. That invariance leads to integrability conditions which play a nontrivial role in the scheme by providing consecutive corrections to the velocity of the interface. Its direct consequence is the fact that operator $\mathcal{L}(\hat{q}_0)$ has an eigenfunction belonging to the eigenvalue equal to zero (the so-called zero mode). Indeed, by differentiating Eq. (20) with respect to s one obtains

$$\hat{\mathcal{L}}(\hat{q}_0)\left[\frac{d\hat{q}_0}{ds}\right] = \mathbf{0}, \tag{22}$$

which means that $\hat{q}_r = d\hat{q}_0/ds$ is the right translational zero mode. The operator $\mathcal{L}(\hat{q}_0)$ has in addition the left translational zero mode which is different from its right counterpart as the operator is not self-conjugate. It can be easily verified that the mode has the following form $\hat{q}_l = \exp[2(2\alpha-1)s]\hat{q}_r$. Let us multiply both sides of Eq. (21) by $\hat{q}_l$, take the trace, and integrate over s. On carrying out integration by parts on the lhs of the resulting equation one obtains the following identity:

$$\frac{1}{2}\left\{ e^{2(2\alpha-1)s}\,\mathrm{Tr}\left[\hat{q}_r\frac{d\hat{q}_{(\mu,\nu)}}{ds} - \frac{d\hat{q}_r}{ds}\hat{q}_{(\mu,\nu)}\right]\right\}_{s=-\infty}^{s=+\infty} + \int_{-\infty}^{+\infty} ds\,\mathrm{Tr}\{\hat{q}_{(\mu,\nu)}\hat{\mathcal{L}}(\hat{q}_0)[\hat{q}_r]\} = \int_{-\infty}^{+\infty} ds\,\mathrm{Tr}[\hat{q}_l\,\hat{\mathcal{N}}_{(\mu,\nu)}]. \tag{23}$$

The lhs of Eq. (23) vanishes for the values of α in the interval of interest (0, 1). One thus arrives at the crucial ingredient of the perturbative scheme, i.e., the set of nontrivial integrability conditions that must be satisfied by the successive corrections $\hat{q}_{(\mu,\nu)}$ to the order parameter

$$\int_{-\infty}^{+\infty} ds\,\mathrm{Tr}[\hat{q}_l\,\hat{\mathcal{N}}_{(\mu,\nu)}] = 0. \tag{24}$$

The translational symmetry is not the only one present in the model. Apart from the translational zero modes $\hat{q}_r$, $\hat{q}_l$, the operator $\mathcal{L}(\hat{q}_0)$ possesses also rotational zero modes. The existence of those zero modes is due to the full rotational symmetry of the unperturbed isotropic model. In general, there are three independent rotational zero modes corresponding to rotations about the three mutually perpendicular axes of the coordinate system. They have the form $\hat{\theta}_i = [\hat{t}_i, \hat{q}_0]$. Matrix $\hat{t}_i$ $(i=1,2,3)$ is the generator of the rotation about the ith axis $[(\hat{t}_i)_{jk} = \epsilon_{ijk}]$. Indeed, one can easily verify that $\mathcal{L}(\hat{q}_0)[\hat{\theta}_i] = [\hat{t}_i, \mathcal{L}(\hat{q}_0)[\hat{q}_0]] = 0$ since expression $\mathcal{L}(\hat{q}_0)[\hat{q}_0]$ vanishes being identical to the rhs of Eq. (20). The corresponding integrability conditions with the rotational zero modes are of lesser importance to the perturbative scheme as they may be shown not to introduce any nontrivial restrictions on the solution. The point is that the particular choice of boundary conditions (see Sec. II) is consistent with the evolution equation. Yet, the modes themselves are of relevance in what follows as the solutions of the homogeneous counterpart of Eq. (21).

B. The zeroth order approximation

The zeroth order contribution must obey Eq. (20) which is the only nonlinear equation in the perturbative scheme. The solution satisfying the appropriate boundary conditions is known to exist [4] provided $v_0 = 1$. It is the purely uniaxial configuration given by the formula

$$\hat{q}_0(s) = \begin{pmatrix} \Phi_0(s) & 0 & 0 \\ 0 & -\frac{1}{2}\Phi_0(s) & 0 \\ 0 & 0 & -\frac{1}{2}\Phi_0(s) \end{pmatrix}, \tag{25}$$

where $\Phi_0(s) = \frac{1}{2}(1+\tanh s)$. The solution given by Eq. (25) smoothly interpolates between the local minima of the free energy corresponding to the isotropic liquid and nematic phase. The boundary layer is well-defined, its width is of the order of the characteristic length $\xi_{\parallel}$. Note that $\xi_{\parallel}$ is temperature-dependent, see formula (16), and the interface shrinks as the temperature is lowered.

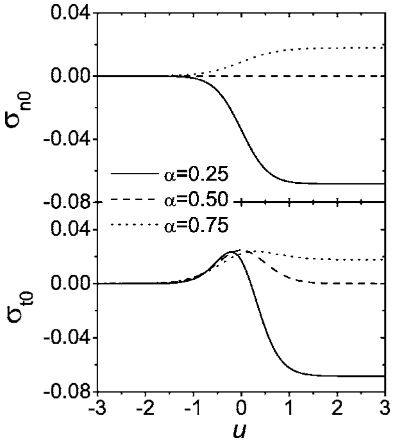

FIG. 1. The zeroth order contributions to the free energy density (bottom) and to the normal component of the strain tensor (top) for the planar interface with the in-plane alignment of the optical axis. Instead of s a different temperature-independent variable is used: $u=\xi/\xi_{\parallel}(1/2,\varepsilon_2)=2(1+\alpha)s/3$. The profiles of the strain tensor components become more dispersed with increasing temperature. The maxima of the free energy density shift always towards the retreating phase, taking the central position of $u=0$ for the static interface.

The strain tensor in the zeroth order approximation $\hat{\Sigma}_0$ is diagonal with $(\hat{\Sigma}_0)_{11}=(\hat{\Sigma}_0)_{22}\neq(\hat{\Sigma}_0)_{33}$. Let us introduce the following notation $\Sigma_{t0}\equiv(\hat{\Sigma}_0)_{11}=(\hat{\Sigma}_0)_{22}$ and $\Sigma_{n0}\equiv(\hat{\Sigma}_0)_{33}$. From definition (8) follows immediately that the transverse component Σ_{t0} is equal to the free energy density of the interface, whereas the normal one Σ_{n0} corresponds to the distribution of the driving strain. Let us introduce dimensionless quantities by the formulas $\Sigma_{t0}=\mathcal{B}^4/(144\mathcal{C}^3)\sigma_{t0}$, $\Sigma_{n0}=\mathcal{B}^4/(144\mathcal{C}^3)\sigma_{n0}$. For both σ_{t0} and σ_{n0} exact formulas can be easily obtained. We only note that $\sigma_{n0}\sim(2\alpha-1)$ so that for $\alpha=1/2$ $(T=T_{NI})$ the normal component of the strain tensor vanishes. It is consistent with the fact that at the clearing point the nematic and isotropic liquid phases are in a state of thermodynamical equilibrium and the solution given by Eqs. (25) corresponds to a static interface. For $\alpha\neq 1/2$ one of those phases is stable, whereas the other is metastable thus leading to the appearance of the thermodynamical driving force. The counteraction of the friction processes results in the interface propagating at a constant rate. Figure 1 shows the free energy density and the normal strain component in the zeroth order approximation for three indicated values of temperature.

C. The first order correction

The consecutive corrections to the order parameter are elements of the space of symmetric and traceless matrices 3×3 and can be uniquely represented by its components in a basis of that space of which we make a special choice

$$\hat{E}_1=\frac{1}{\sqrt{6}}\begin{pmatrix}2&0&0\\0&-1&0\\0&0&-1\end{pmatrix},\quad \hat{E}_2=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&0\\0&1&0\\0&0&-1\end{pmatrix},$$

$$\hat{E}_3=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix},\quad \hat{E}_4=\frac{1}{\sqrt{2}}\begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix},\tag{26}$$

$$\hat{E}_5=\frac{1}{\sqrt{2}}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}.$$

The normalization constants are such that $\mathrm{Tr}(\hat{E}_a\hat{E}_b)=\delta_{ab}$, where δ_{ab} is the Kronecker tensor, and $a,b\in\{1,2,3,4,5\}$. Then $\hat{q}_{(\mu,\nu)}$ reads

$$\hat{q}_{(\mu,\nu)}=q^a_{(\mu,\nu)}\hat{E}_a,\tag{27}$$

where the Einstein summation rule has been adopted. The linear operator $\hat{\mathcal{L}}(\hat{q}_0)$ is represented in basis (26) by a 5×5 symmetric matrix whose elements are given by the formula $[\mathcal{L}(\hat{q}_0)]^a_b=\mathrm{Tr}\{\hat{E}_a\hat{\mathcal{L}}(\hat{q}_0)[\hat{E}_b]\}$. Using Eqs. (A1) and (25) one can show that $\hat{\mathcal{L}}(\hat{q}_0)=\mathrm{diag}[\mathcal{L}_1,\mathcal{L}_2,\mathcal{L}_2,\mathcal{L}_3,\mathcal{L}_3]$, where

$$\mathcal{L}_1=\frac{1}{2}\frac{d^2}{ds^2}+(2\alpha-1)\frac{d}{ds}-4\alpha+8(1+\alpha)\Phi_0-12\Phi_0^2,\tag{28}$$

$$\mathcal{L}_2=\frac{1}{2}\frac{d^2}{ds^2}+(2\alpha-1)\frac{d}{ds}-4\alpha-8(1+\alpha)\Phi_0-4\Phi_0^2,\tag{29}$$

$$\mathcal{L}_3=\frac{1}{2}\frac{d^2}{ds^2}+(2\alpha-1)\frac{d}{ds}-4\alpha+4(1+\alpha)\Phi_0-4\Phi_0^2.\tag{30}$$

The components $q^a_{(\mu,\nu)}$ are thus solutions of a set of five decoupled linear ordinary differential equations of the form

$$[\mathcal{L}(\hat{q}_0)]^a_b q^b_{(\mu,\nu)}=\mathcal{N}^a_{(\mu,\nu)},\tag{31}$$

where

$$\mathcal{N}^a_{(\mu,\nu)}=\mathrm{Tr}(\hat{\mathcal{N}}_{(\mu,\nu)}\hat{E}_a).\tag{32}$$

Equations (31) can be solved by the standard Green function method [26] provided one determines the boundary conditions. Let us hence note that the zeroth order solution, cf. Eqs. (25), saturates the values implied by the corresponding boundary conditions discussed in Sec. II. This in turn uniquely determines the boundary conditions for the higher order corrections:

$$\lim_{s\to\pm\infty}\hat{q}_{(\mu,\nu)}(s)=\mathbf{0}.\tag{33}$$

Now we are ready to calculate the first order corrections to the velocity and the order parameter of the interface. First, from Eqs. (25), (A2), and (A3) we find the inhomogeneous terms $\hat{\mathcal{N}}_{(1,0)}$ and $\hat{\mathcal{N}}_{(0,1)}$. From the only nontrivial integrability condition (24) one obtains the following first order corrections to the velocity of the interface:

$$\upsilon_{(1,0)} = -\frac{1}{6}, \quad \upsilon_{(0,1)} = -\frac{1}{8}(2\alpha+1). \tag{34}$$

The only nonvanishing components of $\hat{\mathcal{N}}_{(1,0)}$ and $\hat{\mathcal{N}}_{(0,1)}$ are those with $a=1,2$, so one obtains inhomogeneous equations for the two corresponding components of the first order corrections only. For the sake of clarity of final formulas let us introduce the following notation: $q^1_{(1,0)}=\sqrt{6}/2\Psi_1$, $q^2_{(1,0)}=\sqrt{2}/2\Psi_2$, $q^1_{(0,1)}=\sqrt{6}/2\Lambda_1$, $q^2_{(0,1)}=\sqrt{2}/2\Lambda_2$. Now, using Eqs. (31) and Appendix B one can find the appropriate solutions. While the solutions for Ψ_2 and Λ_2 functions have to be calculated numerically for every value of α, the functions Ψ_1 and Λ_1 can be shown to reduce to the following explicit formulas: $\Psi_1(s)=s/(12\cosh^2 s)$, $\Lambda_1(s)=[(2\alpha-1)s-2\ln(1-\tanh s)]/(16\cosh^2 s)$. Thus the particular solution for the total first order correction to the order parameter reads

$$\hat{q}_1(s) = \frac{\sqrt{6}}{2}[\varepsilon_2\Psi_1(s)+\varepsilon_3(\alpha)\Lambda_1(s)]\hat{E}_1 + \frac{\sqrt{2}}{2}[\varepsilon_2\Psi_2(s) + \varepsilon_3(\alpha)\Lambda_2(s)]\hat{E}_2. \tag{35}$$

Let us now show that Eq. (35) gives, in fact, the final solution for $\hat{q}_1$. The general solution of Eq. (21) is obtained by adding the general solution of its homogeneous counterpart to the particular solution. The diagonal structure of the operator $\hat{\mathcal{L}}(\hat{q}_0)$ implies that the solution will involve pairs of linearly independent solutions of the homogeneous equations with the operators $\mathcal{L}_i$, where $i=1,2,3$, which are listed in Appendix B. The general solution of the homogeneous equation $\hat{q}_h(s)$ is thus given by the following formula:

$$\begin{aligned}\hat{q}_h(s) &= [A_1\Phi_1(s)+A_2\Phi_2(s)]\hat{E}_1 + [B_1\Xi_1(s)+B_2\Xi_2(s)]\hat{E}_2 \\ &\quad + [C_1\Xi_1(s)+C_2\Xi_2(s)]\hat{E}_3 + [D_1\Theta_1(s)+D_2\Theta_2(s)]\hat{E}_4 \\ &\quad + [F_1\Theta_1(s)+F_2\Theta_2(s)]\hat{E}_5.\end{aligned} \tag{36}$$

Now, the constants A_2, B_1, B_2, C_1, C_2, D_2, and F_2 must vanish since the corresponding solutions are not bounded. The contributions introduced by D_1 and F_1 are related to the two nontrivial rotational zero modes $\hat{\theta}_i(s)$ $(i=2,3)$. Adding those terms to the particular solution would be equivalent to the uniform rotation of the optical axis about the second and third axis of the coordinate system, respectively. Yet, the boundary conditions exclude such rotations, hence $D_1=F_1=0$. Similarly, the constant A_1 introduces the translational zero mode $\hat{q}_r$ into the solution, note that $\Phi_1(s)=d\Phi_0(s)/ds$. The boundary conditions fail to fix the value of A_1. The solution $\hat{q}(s)$ is thus not determined uniquely, which is due again to the invariance with respect to the translations in s. In order to obtain a unique solution we have to impose an additional condition. We thus require that

$$\mathrm{Tr}(\hat{q}(0)\hat{E}_1) = \mathrm{Tr}(\hat{q}_0(0)\hat{E}_1), \tag{37}$$

where $\hat{q}_0(s)$ is a concrete, explicitly given tensor describing the unperturbed interface with a fixed location on the s axis. The condition in Eq. (37) breaks the translational invariance and implies $q^1_{(\mu,\nu)}(0)=0$ for $\mu+\nu \geqslant 1$. From Eq. (35) it follows that $q^1_1(0)=0$, which leads to $A_1=0$. We have thus shown that for the boundary condition (33) supplemented with the above condition one obtains a unique interface solution whose form up to the first order is given by Eq. (35). The functions Ψ_1, Λ_1 correct the profile of the scalar order parameter, whereas Ψ_2, Λ_2 introduce the biaxiality. Let us note that there is no reorientation of the optical axis in the boundary layer in this order. Moreover, by inspection of the inhomogeneous term given by Eqs. (A2) and (A3) it can be shown that the orientational modes will not appear in any higher order of the perturbative series. Figure 2 shows the functions Ψ_i and Λ_i $(i=1,2)$ for three indicated values of temperature.

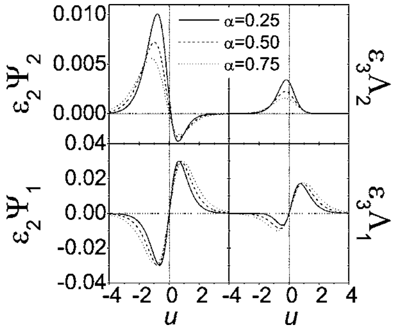

FIG. 2. First order corrections to the order parameter, cf. Eq. (35). Coordinate u as in Fig. 1. The corrections do not exceed 4% of the amplitude of the zeroth order contribution (~ 1) justifying the perturbative approach.

It can be shown that the total first order correction $\hat{\Sigma}_1$ to the strain tensor is diagonal. Hence we introduce the notation analogous to that in the zeroth order, i.e., $\Sigma_t^{(\mu,\nu)}=\mathcal{B}^4/(144\mathcal{C}^3)\sigma_t^{(\mu,\nu)}$, $\Sigma_n^{(\mu,\nu)}=\mathcal{B}^4/(144\mathcal{C}^3)\sigma_n^{(\mu,\nu)}$. Again explicit analytical formulas for the first order corrections $(\mu+\nu=1)$ can be obtained, and like in the zeroth order both $\sigma_n^{(1,0)}$ and $\sigma_n^{(0,1)}$ vanish for $\alpha=1/2$. Figure 3 shows functions $\sigma_t^{(\mu,\nu)}(u)$ and $\sigma_n^{(\mu,\nu)}(u)$ $(\mu+\nu=1)$ for three indicated values of α.

IV. THE INTERFACE STRUCTURE FOR THE HOMEOTROPIC ALIGNMENT

The issue of the planar interface in nematic liquid crystals would not be complete without a reference to the homeotro-

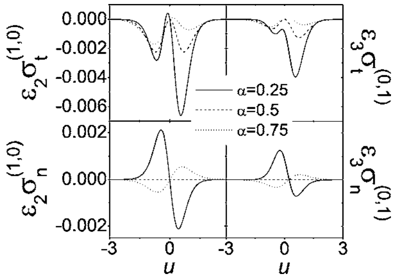

FIG. 3. The first order corrections to the free energy density (bottom) and to the normal component of the strain tensor (top) for the planar interface with the in-plane alignment of the optical axis. Coordinate u as in Fig. 1. The corrections are asymptotically zero, which is due to the fact that the elastic perturbation (14) does not affect the vacuum manifold.

pic configuration. It is true that it has been proved to be stable only in the less physical case of $L_2 < 0$, but still an experimental setup where the alignment of the optical axis could be controlled is conceivable. The construction of the perturbative scheme goes along analogous lines as those for the in-plane alignment, the main difference is that the zeroth order solution now corresponds to $L_2 \neq 0$. One can show that in the dimensionless variables defined by the following formulas

$$\xi = \xi_{\perp}(\alpha,\varepsilon_2)s, \quad \xi_{\perp}(\alpha,\varepsilon_2) = \sqrt{\frac{6+\varepsilon_2}{3(2-\varepsilon_2)}}\xi_0(\alpha),$$
$$\mathcal{V}_{\perp}(\alpha,\varepsilon_2) = \sqrt{\frac{6+\varepsilon_2}{3(2-\varepsilon_2)}}\mathcal{V}_0(\alpha)\upsilon_{\perp} \tag{38}$$

the equation of motion can be rewritten as

$$\frac{1}{2}\frac{d^2 q_{ij}}{ds^2} + (2\alpha - 1)\upsilon^{\perp}\frac{dq_{ij}}{ds} - 4\alpha q_{ij} + 8(1+\alpha)\hat{q}_{ij}^2 - \frac{8}{3}\operatorname{Tr}\hat{q}^2 q_{ij} - \frac{8}{3}(1+\alpha)\operatorname{Tr}\hat{q}^2\delta_{ij} - \frac{1}{4}\varepsilon_3^{\perp}\left[3\frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{i3}\delta_{j3} - 6\frac{d}{ds}\left(q_{33}\frac{dq_{ij}}{ds}\right) - \frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{ij}\right] = 0, \tag{39}$$

where $\varepsilon_3^{\perp} = L_3 S_0/(3L_1 + 2L_2)$ serves now as the only expansion parameter. Let us only quote the most important results. The zeroth order solution has the form $q_0^{\perp}(s) = \operatorname{diag}[-1/2\Phi_0(s), -1/2\Phi_0(s), \Phi_0(s)]$, where Φ_0 is given in Eq. (25), and $\upsilon_0^{\perp} = 1$. Although in the dimensionless variables the solution is given by exactly the same set of formulas as that in the zeroth order approximation of the parallel alignment interface, they are physically nonequivalent. The corresponding lengths scales and velocities are different, cf. Eqs. (16), (17), and (38). The first order correction to the interface velocity reads $\upsilon_1^{\perp} = -3\upsilon_{(0,1)}$, where $\upsilon_{(0,1)}$ is given in Eq. (34). The first order correction to the order parameter consistent with the boundary conditions assumed in Sec. II reads

$$\hat{q}_1^{\perp}(s) = -\frac{3\sqrt{6}}{2}\varepsilon_3^{\perp}\Lambda_1(s)\hat{E}_1^{\perp}, \tag{40}$$

where the function Λ_1 is given in Sec. III C, and $\hat{E}_1^{\perp} = 1/\sqrt{6}\operatorname{diag}[-1,-1,2]$. Let us note that biaxiality is absent in the first order. Moreover, it can be easily shown that inserting into Eq. (39) a purely uniaxial ansatz leads to a single ordinary differential equation in s for the scalar order parameter, which implies that no biaxiality as well as reorientation of the optical axis will appear for that configuration. The strain tensor in the present case may be shown to be diagonal. The transverse and normal components in the zeroth order are exactly the same as for the in-plane alignment. The first order corrections differ only by a constant factor, i.e., $\sigma_{t1}^{\perp} = -3\sigma_t^{(0,1)}$, $\sigma_{n1}^{\perp} = -3\sigma_n^{(0,1)}$.

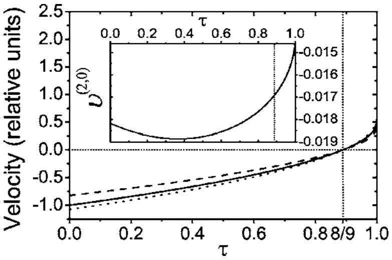

FIG. 4. Temperature dependence of the interface velocity for the in-plane (dashed line) and homeotropic (dotted line) alignment calculated up to the first order. The solid line shows the velocity of the unperturbed interface $\mathcal{V}_{\|(\perp)0}(\tau)$ which is equivalent to the de Gennes' variational solution. $|\mathcal{V}_{\|(\perp)0}(0)|$ has been chosen as the velocity unit. In the inset temperature dependence of the second order correction to the interface velocity is depicted. The parameter values adopted in the calculations are those of PAA.

V. DISCUSSION

In Secs. III and IV the solutions of the pertinent evolution equation corresponding to the moving planar interface with the in-plane and homeotropic alignment, respectively, have been provided. To obtain the solutions a systematic and consistent perturbative scheme has been constructed. It allows one to calculate order by order the corrections to the order parameter field. The consistency conditions given in Eq. (24) are its crucial component yielding the corrections to the interface velocity.

Now, let us focus on the features revealed with the help of that scheme. Firstly, using the elastic parameters for PAA the velocity vs temperature curves were calculated, see Fig. 4. There is a substantial reduction of $\mathcal{V}_{\|}$ compared to the de Gennes solution. In [27] this was shown for $L_2 \neq 0$ only, and here we extend that result for the case where the full elastic anisotropy of the nematic liquid crystal is taken into account ($\upsilon^{(1,0)}, \upsilon^{(0,1)} < 0$). At the same time it is revealed that for the homeotropic configuration the elastic anisotropy has the opposite effect on the interface velocity ($\upsilon_{\perp}^{(0,1)} > 0$), although the change measured relative to the de Gennes solution is smaller. Let us also point out that it would be of interest to set up an experiment in which the alignment of the optical axis at the interface could be controlled. Then, given the rather strong dependence of $\mathcal{V}_{\|}/\mathcal{V}_{\perp}$ on ε_2 the ratio of the de Gennes' elastic constants L_2/L_1 could be estimated. The first order corrections to the interface velocity for the homeotropic and in-plane alignment are temperature dependent (α-dependent). Let us note, however, that for nematogens with the splay and bend elastic constants nearly equal [e.g., p, p'-dibutylazoxybenzene (DIBAB) at transition temperature $\simeq 320$ K, $K_{11} = 4.8$, $K_{22} = 3.0$, $K_{33} = 4.7$ in 10^{-12} N [22]], i.e., where the ratio $L_3 S_0/L_2$ ($\simeq 0.02$ for DIBAB) is negligibly small the first order velocity correction does not depend on temperature, see Eq. (34) (for the in-plane configuration), or vanishes (for the homeotropic alignment). Having found the first order correction to the order parameter (35), the second order correction $\upsilon^{(2,0)}$ to the interface velocity could be calculated, using Eqs. (A2) and (A3) and the consistency condition (24). The inset in Fig. 4 shows the

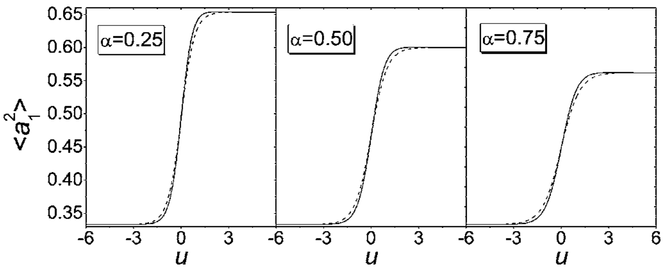

FIG. 5. The orientational structure of the planar interface with the in-plane alignment of the director in terms of the mesoscopic average $\langle a_1^2 \rangle$, where versor $\hat{a}$ parametrizes the orientation of a molecule's long axis. Coordinate u as in Fig. 1. The solid line was obtained within the first order approximation, whereas the dashed curve corresponds to the unperturbed uniaxial ansatz. There is an apparent enhancement of order to the N-phase side, accompanied by its relatively weaker reduction on the I-phase side. In every temperature regime no shift of the scalar order parameter profile occurs.

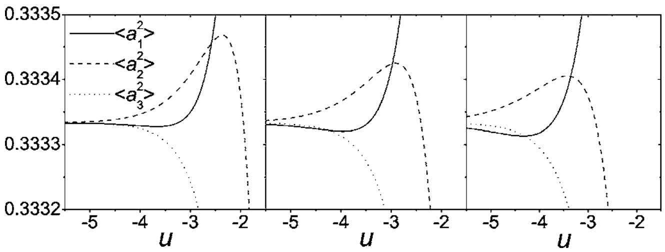

FIG. 6. The orientational structure of the planar interface with the in-plane alignment of the director in terms of the mesoscopic averages $\langle a_i^2 \rangle$, where versor $\hat{a}$ parametrizes the orientation of a molecule's long axis. Coordinate u as in Fig. 1. The symmetry restoring feature observed on the I-phase side (negative u) is shown. As temperature rises the feature becomes more diffused and shifts deeper into the isotropic phase. The ordering state when one moves from the center of the interface toward its I-phase side changes to uniaxial with the director at right angles to that on the N-phase side, and only afterwards becomes fully isotropic. The transition between the two in-plane directions occurs through the point where the $\langle a_1^2 \rangle$ and $\langle a_2^2 \rangle$ curves intersect and the order is planar (oblate) uniaxial (negative scalar order parameter).

corresponding result. One can see that $\upsilon^{(2,0)}$ displays a rather weak temperature dependence. The maximum relative change in the velocity magnitude due to that dependence can be shown not to exceed 1%. This implies that for nematogens with a small difference of the splay and bend elastic constants the temperature dependence of the interface velocity is predominantly determined by the bulk properties of the nematic liquid crystal and is given by the well-known formula $\mathcal{V}=C[1-3\sqrt{1-\tau}]$, where C is a material constant. The dependence of C on the elastic constants L_1 and L_2 is given explicitly by Eq. (38) for the homeotropic alignment and by the approximate formula $C_{\parallel} \simeq \sqrt{2/[L_1(2-\varepsilon_2)]}[1-\varepsilon_2/6 -0.017\varepsilon_2^2]$ for the in-plane configuration.

The results revealing the ordering structure of the interface are noteworthy. First let us discuss the energetically favorable case of the in-plane alignment. For the sake of clarity of presentation we shall refer to the microscopic definition of the underlying order parameter. It arises in that formulation as the quadrupolar term of the probability density distribution $P(\hat{a},\vec{r}) \approx 1/(4\pi)\{1+5\hat{Q}(\vec{r})\circ(\hat{a}\otimes\hat{a})\}$, where $\hat{a}$ denotes a unit vector parametrizing the orientation of a molecule's long axis. The first order term in the above expansion vanishes due to the up-down symmetry of the constituent molecules. The normalization of the distribution implies that $\hat{Q}$ should be traceless. Further, it is easily shown that if the order parameter is at some point diagonal and $\hat{Q}(\vec{r})=\mathrm{diag}[\lambda_1,\lambda_2,\lambda_3]$ then the corresponding values of the mesoscopic averages $\langle a_i^2 \rangle$ $(i=1,2,3)$ at that point are related to the eigenvalues by the symmetric formula $\langle a_i^2 \rangle=(1+2\lambda_i)/3$. Using the solution up to the first order, cf. Eqs. (25) and (35), and adopting the parameter values of PAA we calculated the orientational structure of the interface. Figure 5 shows the values of $\langle a_1^2 \rangle$ across the interface. Furthermore, the most striking feature appears to the I-phase side, whether advancing or retreating, which is depicted in Fig. 6 in terms of the mesoscopic averages $\langle a_i^2 \rangle$. This type of interpolation restoring the symmetry in the phase boundary turns out to be energetically preferable to the reorientation of the director expected in [4]. Such a feature was obtained also in numerical calculations of the interface profile in the two-constant approximation [7]. The relaxation of the splay-bend degeneracy further enhances it. This can be seen by considering the corresponding contributions to the biaxiality. Figure 7 shows the biaxiality degree in terms of the difference $\langle a_2^2 \rangle - \langle a_3^2 \rangle$. The biaxiality induced by the L_3-term is positive and shifted towards the isotropic phase (cf. the functions Ψ_2 and Λ_2 in Fig. 2).

The structure of the interface with the homeotropic alignment calculated up to the first order is purely uniaxial. Figure 8 depicts its ordering structure. Our results are consistent with those obtained within statistical-molecular approach [13,5]: no biaxiality for the homeotropic alignment and the occurrence of it for the parallel alignment with a pronounced maximum on the I-side of the interface. In contrast to the previous results, obtaining the biaxiality profile here involves only one-dimensional integrating which can be readily performed with mathematical software. That facilitates the comparison of that result with the prospective experimental data.

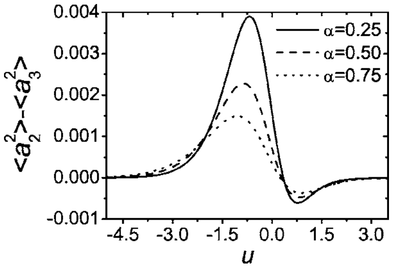

FIG. 7. The biaxiality degree of the in-plane configuration in terms of the difference $\langle a_2^2 \rangle - \langle a_3^2 \rangle$, where versor $\hat{a}$ parametrizes the orientation of a molecule's long axis. Coordinate u as in Fig. 1. The amplitude of that effect increases monotonically as temperature is lowered. It is asymmetric with the pronounced maximum on the I-phase side. On the N-phase side the orientational distribution of molecules is slightly tilted towards the x^3-axis, which is exclusively due to the L_2-term of the free energy density (cf. the function Ψ_2 in Fig. 2).

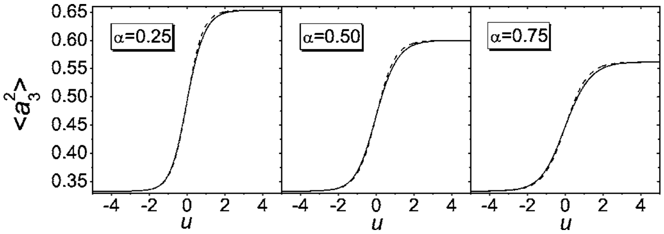

FIG. 8. The orientational structure of the planar interface with the homeotropic alignment of the director in terms of the mesoscopic average $\langle a_3^2 \rangle$, where versor $\hat{a}$ parametrizes the orientation of a molecule's long axis. Coordinate u as in Fig. 1. The solid line was obtained within the first order approximation, whereas the dashed curve corresponds to the unperturbed ansatz. The degree of ordering is decreased on the N-phase side. The change is opposite on the I-phase side, but its magnitude is significantly lower. There is no shift of the scalar order parameter profile.

In the free energy profile of a moving interface, see Fig. 9, a humplike structure is present with the peak of the free energy density shifted towards the retreating phase. The first order corrections in Fig. 3 are negative and they vanish asymptotically. The former feature is due to the reduction of the elastic free energy by the anisotropic perturbation (14), whereas the latter one is attributable to the fact that the elastic energy terms do not modify the equilibrium value of the ordering degree S_0. The magnitude of the corrections is a decreasing function of temperature. Even for the static interface ($\alpha=1/2$) its profile is an asymmetric two-peak structure which is larger on the advancing phase side. Figure 9 shows clearly that such a shape, contrary to what might be expected, does not lead to the splitting of the free energy profile, but results mainly in its steepening. This is again consistent with the elastic free energy reduction as compared to the unperturbed solution. The reduction of the free energy is distributed in an asymmetric way around the interface center. It is larger on the side of the advancing phase. It remains asymmetric even for the static interface ($\alpha=1/2$), being slightly larger on the nematic-phase side. That result seems not to agree with [7], however, it was the deviation of the free energy density from that given by the de Gennes variational solution that was reported by the authors, whereas here the zeroth order "isotropic" solution has been employed as the reference point. Moreover, a slight depression in the free energy profile on the nematic-phase side appears. To visualize it more clearly we calculated the excess free energy $\Sigma_t - \Sigma_n$ (surface tension) assuming $\varepsilon_3=S_0$ shown in Fig. 10. The correction to the driving force distribution given by the normal component of the strain tensor, see Fig. 3, indicates the appearance of compressive forces for the nematic phase advancing, while a relatively weaker decompression for the opposite case. For the static interface the driving force vanishes. The integrals of the normal components give the net correction to the driving force. It is interesting that in the two-constant approximation these corrections vanish, but relaxing the splay-bend degeneracy leads to nonzero contributions always lowering the driving force. Finally, Fig. 11 shows the temperature dependence of the excess free energy.

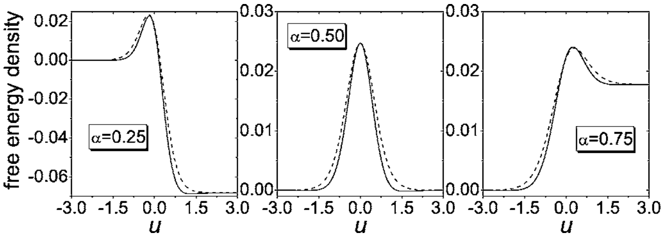

FIG. 9. The free energy density profiles [in units $\mathcal{B}^4/(144\mathcal{C}^3)$] as calculated up to the first order of the perturbative series (solid lines) and those corresponding to the unperturbed solution (dashed lines) for the in-plane alignment of the director at the interface. Coordinate u as in Fig. 1.

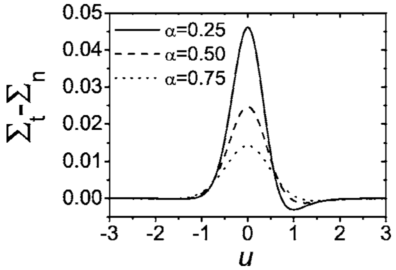

FIG. 10. Excess free energy density [in units $\mathcal{B}^4/(144\mathcal{C}^3)$] as calculated up to the first order of the perturbative series with $\varepsilon_2=0.8$ and $\varepsilon_3=S_0(\alpha)$. Coordinate u as in Fig. 1. There is a slight depression in the free energy density on the N-phase side. This feature is most clear when the nematic phase advances and diminishes with increasing temperature.

In the case of the homeotropic alignment the behavior is the opposite (the corrections change the sign). Figure 12 shows the free energy density profiles obtained with the solution up to the first order. Let us repeat that for this configuration only the corrections from the L_3-term of the elastic free energy are involved. The correction to the free energy is always positive with its magnitude decreasing with temperature. The increase of the elastic energy is related to the apparent increase of elasticity due to lifting the splay-bend degeneracy. A higher level of elasticity is also responsible for the more gradual changes of the free energy density and order parameter across the interface. For the nematic phase

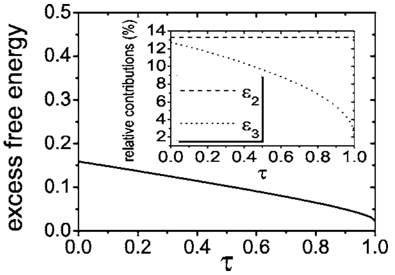

FIG. 11. Excess free energy [in units $[1+L_2/(2L_1)]^{1/2}\mathcal{B}^4\xi_0(1/2)/(216\mathcal{C}^3)$] vs reduced temperature. Inset: The relative reduction rates of the free energy from the two anisotropic elastic terms. The correction introducing the twist anisotropy contributes at a constant rate and dominates in the region around the equilibrium temperature ($\tau=8/9$). The relative contribution from the correction lifting the splay-bend degeneracy increases with decresing temperature becoming finally comparable to the former one.

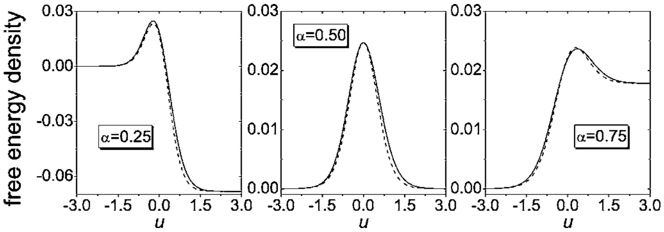

FIG. 12. The free energy density profiles [in units $\mathcal{B}^4/(144\mathcal{C}^3)$] as calculated up to the first order of the perturbative series (solid lines) and those corresponding to the unperturbed solution (dashed lines) for the homeotropic alignment of the director at the interface. Coordinate u as in Fig. 1. The corrections are clearly asymmetric, the changes on the N-phase side are more pronounced. The correction to the free energy is always positive with its magnitude decreasing with temperature.

advancing the boundary region experiences a decompression in the normal direction, whereas, when the isotropic phase is advancing the compression takes place, cf. Fig. 3. In both cases the net driving force is increased.

And finally, let us compare the free energy content (surface tension) of both types of the planar interface at the clearing point, i.e., for $\alpha=\frac{1}{2}$, where the solutions correspond to the static interface. A straightforward calculation gives the following surface tension difference up to the first order:

$$\delta f = f_{\parallel} - f_{\perp} = -\frac{1}{5832}\frac{\mathcal{B}^4\xi_0(1/2)}{\mathcal{C}^3}\left[\frac{1}{3}\varepsilon_2 + \varepsilon_3 + \cdots\right]. \quad (41)$$

Equation (41) indicates that the elastic anisotropy related to L_3 also stabilizes the in-plane configuration, as typically positive values of L_3 are expected.

VI. FINAL REMARKS

The analytical description of the structure of a planar interface in nematic liquid crystals within the framework of the effective TDGL model has been reported. The effects of the full elastic anisotropy on the structure of the interface with the in-plane or homeotropic director alignment are obtained through construction of a consistent perturbative scheme. Within that scheme one can systematically calculate consecutive corrections to the profile and velocity of the interface. The corrections are given either in the explicit form or in terms of one-dimensional integrals which can be easily reproduced. The solutions revealed interesting features of the structure and kinematics of slowly moving or static N/I interfaces.

We have not carried out a rigorous mathematical investigation of the problem of convergence of the perturbative series, as it does not belong to the scope of our work. However, the first order corrections to the order parameter do not exceed 4% of the amplitude of the isotropic approximation. That does not necessarily mean that the series is convergent; it can belong to a wider class of asymptotic series, which is acceptable from the physical viewpoint.

The present approach does not take into account the coupling between the order parameter and the hydrodynamic degrees of freedom. When the Ericksen number is comparable to unity, the coupling between mass flow and orientational degrees of freedom can no more be neglected and the full nematodynamic equations should be solved. Then even the asymptotic bulk states may involve biaxial mode and the reorientation of the optical axis within the boundary layer may occur.

The analytical results reported in the present paper provide a starting point to the more complex problem of the evolution of curved interfaces. Research into that problem may yield valuable insights into the physics of phase transitions involving media with nontrivial intrinsic symmetries [28,29].

ACKNOWLEDGMENTS

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APPENDIX A: THE EQUATION OF MOTION FOR THE CONSECUTIVE CORRECTIONS

The equation governing the shape of the corrections $\hat{q}_{(\mu,\nu)}$ is given by the formula (21), where the linear operator $\hat{\mathcal{L}}(\hat{q}_0)$ reads

$$\hat{\mathcal{L}}(\hat{q}_0)[\hat{q}] = \frac{1}{2}\frac{d^2\hat{q}}{ds^2} + (2ha-1)v_0\frac{d\hat{q}}{ds} - 4\alpha\hat{q} + 8(1+\alpha)(\hat{q}_0\hat{q}+\hat{q}\hat{q}_0) - \frac{16}{3}\,\mathrm{Tr}(\hat{q}_0\hat{q})\hat{q}_0 - \frac{8}{3}(\mathrm{Tr}\,\hat{q}_0^2)\hat{q} - \frac{16}{3}(1+\alpha)\mathrm{Tr}(\hat{q}_0\hat{q})I, \quad (A1)$$

and the inhomogeneous term $\hat{\mathcal{N}}_{(\mu,\nu)}$ can be obtained from the following formal recipe:

$$\hat{\mathcal{N}}_{(\mu,\nu)} = \frac{1}{\mu!\,\nu!}\left.\frac{\partial^{\mu+\nu}\mathcal{G}(\hat{q},v)}{\partial\varepsilon_2^{\mu}\partial\varepsilon_3^{\nu}}\right|_{\varepsilon_2=\varepsilon_3=0}, \quad (A2)$$

where

$$\mathcal{G}(\hat{q},v) = -8(1+\alpha)\hat{q}^2 + \frac{8}{3}\,\mathrm{Tr}(\hat{q}^2)\hat{q} + \frac{8}{3}(1+\alpha)\mathrm{Tr}(\hat{q}^2)I + 8(1+\alpha)(\hat{q}\hat{q}_0+\hat{q}_0\hat{q}) - \frac{8}{3}\,\mathrm{Tr}(\hat{q}_0^2)\hat{q} - \frac{16}{3}\,\mathrm{Tr}(\hat{q}_0\hat{q})\hat{q}_0 - \frac{16}{3}(1+\alpha) \times\mathrm{Tr}(\hat{q}\hat{q}_0)I - 8(1+\alpha)\hat{q}_0^2 + \frac{16}{3}\,\mathrm{Tr}(\hat{q}_0^2)\hat{q}_0 + \frac{8}{3}(1+\alpha)\mathrm{Tr}(\hat{q}_0^2)I - (2\alpha-1)(v-v_0)\frac{d\hat{q}}{ds} + \frac{1}{6}\varepsilon_2\left[\frac{d^2q_{33}}{ds^2}\delta_{ij} - \frac{3}{2}\left(\delta_{3i}\frac{d^2q_{3j}}{ds^2} + \delta_{3j}\frac{d^2q_{3i}}{ds^2}\right) + \frac{3}{2}\frac{d^2q_{ij}}{ds^2}\right] + \frac{1}{6}\varepsilon_3\left[3\frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{i3}\delta_{j3} - 6\frac{d}{ds}\left(q_{33}\frac{dq_{ij}}{ds}\right) - \frac{dq_{kl}}{ds}\frac{dq_{kl}}{ds}\delta_{ij}\right], \quad (A3)$$

where the arguments $\hat{q}$ and v should be replaced by the expansions given in Eq. (19). Let us also note that due care of the noncommutativity of the order parameter should be taken while performing the differentiation.

APPENDIX B: THE GREEN FUNCTIONS FOR OPERATORS $\mathcal{L}_1$ and $\mathcal{L}_2$

Consider equations of the form

$$\mathcal{L}_i \Psi_i(s) = f_i(s), \tag{B1}$$

where $i=1,2$, operators $\mathcal{L}_1$, $\mathcal{L}_2$ are given by Eqs. (28) and (29), respectively, and it is required that the solutions Ψ_i vanish for $s \to \pm\infty$, cf. Eq. (33). The Green functions which are consistent with the above boundary conditions and correspond to the operators $\mathcal{L}_1$ and $\mathcal{L}_2$, respectively, are given by the formulas

$$G_1(s,\zeta) = \frac{\Phi_2(s)\Phi_1(\zeta)\theta(s-\zeta) - \Phi_1(s)\Phi_2(\zeta)[\theta(s-\zeta) - \theta(-\zeta)]}{\Phi_1(\zeta)\Phi_2'(\zeta) - \Phi_2(\zeta)\Phi_1'(\zeta)}, \tag{B2}$$

$$G_2(s,\zeta) = \frac{\Xi_2(s)\Xi_1(\zeta)\theta(s-\zeta) + \Xi_1(s)\Xi_2(\zeta)\theta(\zeta-s)}{\Xi_1(\zeta)\Xi_2'(\zeta) - \Xi_2(\zeta)\Xi_1'(\zeta)}, \tag{B3}$$

where $\theta(x)$ denotes the Heaviside step function, and the functions Φ_1, Φ_2 and Ξ_1, Ξ_2 are pairs of linearly independent solutions of the corresponding homogeneous differential equations $\mathcal{L}_1\Phi=0$ and $\mathcal{L}_2\Xi=0$. It can be easily verified that

$$\Phi_1(s) = \frac{d\Phi_0(s)}{ds}, \quad \Phi_2(s) = \Phi_1(s)\int_0^s d\sigma e^{-2(2\alpha-1)\sigma}[\Phi_1(\sigma)]^{-2}, \tag{B4}$$

$$\Xi_1(s) = e^{2s}(1+e^{2s})^2,$$
$$\Xi_2(s) = \Xi_1(s)\int_s^{+\infty} d\sigma e^{-2(2\alpha-1)\sigma}[\Xi_1(\sigma)]^{-2}. \tag{B5}$$

The particular solutions of Eqs. (B1) are given by the integrals $(i=1,2)$

$$\Psi_i(s) = \int_{-\infty}^{+\infty} d\zeta G_i(s,\zeta) f_i(\zeta). \tag{B6}$$

Finally, let us quote the pair of linearly independent solutions of the equation $\mathcal{L}_3\Theta=0$

$$\Theta_1(s) = \Phi_0(s), \quad \Theta_2(s) = \Theta_1(s)\int_0^s d\sigma e^{-2(2\alpha-1)\sigma}[\Theta_1(\sigma)]^{-2}, \tag{B7}$$

where $\Phi_0(s)$ is given in Eq. (25).

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