The Isotropic-Nematic Interface with an Oblique Anchoring Condition

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Abstract

We present numerical and analytic results for uniaxial and biaxial order at the isotropic-nematic interface within Ginzburg-Landau-de Gennes theory. We study the case where an oblique anchoring condition is imposed asymptotically on the nematic side of the interface, reproducing results of previous work when this condition reduces to planar or homoeotropic anchoring. We construct physically motivated and computationally flexible variational profiles for uniaxial and biaxial order, comparing our variational results to numerical results obtained from a minimization of the Ginzburg-Landau-de Gennes free energy. While spatial variations of the scalar uniaxial and biaxial order parameters are confined to the neighbourhood of the interface, nematic elasticity requires that the director orientation interpolate linearly between either planar or homoeotropic anchoring at the location of the interface and the imposed boundary condition at infinity. The selection of planar or homoeotropic anchoring at the interface is governed by the sign of the Ginzburg-Landau-de Gennes elastic coefficient $L_2$. Our variational calculations are in close agreement with our numerics and agree qualitatively with results from density functional theory and molecular simulations.

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I. INTRODUCTION

Nematic liquid crystals, typically formed in suspensions of rod-like molecules whose aspect ratio deviates sufficiently from unity, exhibit orientational order in the absence of translational order [1, 2, 3]. Such order is quantified through a traceless, symmetric tensor $Q_{\alpha\beta}$ defined at every point in space [1, 4]. In the nematic phase, the order parameter is

$$Q_{\alpha\beta} = \frac{3S}{2} \left(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}\right) + \frac{T}{2} (l_\alpha l_\beta - m_\alpha m_\beta)$$

(1)

where the director $n$ is defined as the normalized eigenvector corresponding to the largest eigenvalue of $Q$, the subdirector $l$ is associated with the sub-leading eigenvalue, and their mutual normal $m$ is obtained from $n \times l$. The quantities $S$ and $T$ represent the strength of uniaxial and biaxial ordering: $|S| \neq 0$, $T = 0$ is the uniaxial nematic whereas $S, T \neq 0$ with $T < 3S$ defines the biaxial case [1].

The description of the early stages of phase-ordering upon quenches from the isotropic phase, the properties of nematic droplets within the isotropic phase and the structure of the isotropic-nematic interface are all problems which require that nematic and isotropic phases be treated within the same framework. The inhomogeneous order parameter configurations obtained in these cases are weighted by the Ginzburg-Landau-de Gennes (GLdG) free energy, obtained via a gradient expansion in $Q$ in which only low-order symmetry allowed terms are retained [1, 5]. The simplest of the problems above is that of the structure of the infinite, flat isotropic-nematic interface, studied initially by de Gennes [5].

Nematic ordering is strongly influenced by confining walls and surfaces, which impose a preferred orientation or “anchoring condition” on the nematic state. Such a preferred orientation yields an anchoring angle, defined as the angle made by the director in the immediate neighbourhood of the surface with the surface normal. Anchoring normal to the surface is termed as homoeotropic, whereas anchoring in the plane of the surface is termed as planar. The general case is that of oblique anchoring.

As is the case with surfaces, the interface between a nematic and its isotropic phase can also favour a particular anchoring. The problem of interface structure for the nematic is particularly interesting since it illustrates how the structure in the interfacial region can differ substantially from structure in the bulk. It is known, for example, that a region proximate to the interface can exhibit biaxiality within the LGdG theory, even if the stable nematic
phase is pure uniaxial\[6\], provided planar anchoring is enforced. Such biaxiality is absent if the anchoring is homoeotropic\[5\]. These two limits, of homoeotropic and planar anchoring, lead to interface profiles of \(S\) and \(T\) which vary only in the vicinity of the interface, as well as orientations which are uniform across the interface\[5\].

Can oblique anchoring be stabilized, within GLdG theory, at the interface between a bulk uniaxial nematic and its isotropic phase? Suppose we introduce boundary conditions that impose a specified oblique orientation deep into the nematic phase, where the magnitude of the order parameter is saturated. The question, then, is whether such an imposed orientation is relaxed to a preferred value in the vicinity of the interface. The difficulties with this problem stem from the fact that changes in the local frame orientation on the nematic side of the interface come with an elastic cost arising out of nematic elasticity. This is an effect sensitive, in principle, to system dimensions, since gradients can be smoothed out by allowing the changes to occur over the system size. While this cost can be reduced by suppressing the order parameter amplitudes in regions where order parameter phases vary strongly, the precise way in which this might happen, if at all, is an open question.

Popa-Nita, Sluckin and Wheeler (PSW)\[6\] studied this problem numerically within a GLdG approach, using a set of variables \(\eta_s\) and \(\mu_s\) introduced in Ref. \[8\]. These variables are combinations of the variables \(S\), \(T\) and \(\theta\) used in this paper. Although the focus of their study was the emergence of biaxiality at the interface with a planar anchoring condition, PSW remarked that if the asymptotic orientation of the director in the nematic phase was set to any value other than 90° (planar anchoring) or 0 (homoeotropic anchoring) for large \(z\), then \(\eta_s\) and \(\mu_s\) approached this value with non-zero slope. PSW thus concluded that there could be no stable anchoring if the orientation of the director in the nematic phase was neither planar nor homoeotropic, but oblique. The precise nature of the resulting state obtained upon applying an oblique anchoring condition was not addressed by PSW\[6, 7\].

Density functional calculations on hard-rod systems using Onsager’s theory applied to the free isotropic-nematic interface indicate that the minimum surface free energy is obtained when the rods lie parallel to the isotropic-nematic interface, the case of planar anchoring\[9, 10\]. Molecular simulations of a system of hard ellipsoids, in which an anchoring energy fixes the director orientation in the nematic phase at a variety of angles, indicate that the isotropic-nematic interface favours planar anchoring. These simulations, and a mean-field calculation based on the Onsager functional, find that the angle profile is approximately
linear as one moves away from the boundary condition imposed by the wall at one end of the simulation box\cite{11, 12}. These results, in particular concerning the stability of planar anchoring, are consistent with those from other treatments\cite{13, 14, 15, 16, 17}. However, several other papers indicate specific regimes in which homeotropic or oblique anchoring may be stable. Moore and McMullen\cite{18} numerically evaluate the inhomogeneous grand potential within a specific approximation scheme finding that planar anchoring is preferred at the interface for long spherocylinders, but oblique or homeotropic anchoring may be an energetically favourable alternative for smaller aspect ratios. Holyst and Poniewierski study such hard spherocylinders in the Onsager limit, noting that oblique anchoring is favoured over a considerable range of aspect ratios\cite{19}. Finally, experiments provide evidence for both oblique\cite{20} and planar anchoring\cite{21}, with electrostatic effects possibly favouring oblique anchoring.

This paper studies the isotropic-nematic interface within GLdG theory in the case where an oblique anchoring condition is imposed on the nematic state far from the location of the interface. For a flat interface, the components of $Q$ can depend only on the coordinate perpendicular to the interface. We assume that this coordinate is aligned along the $z$ axis, as shown in Fig. 1, which defines the geometry we work with in this paper. We work at phase coexistence, imposing boundary conditions fixing the isotropic phase at $z = -\infty$ and the nematic phase at $z = \infty$. The components of $Q$ as $z \to \infty$ are chosen so that $S$ is fixed to its value at coexistence $S_c$, while the axis of the nematic is aligned along a specified (oblique) direction. The coexisting states must be separated by an interface in which order parameters rise from zero on the isotropic side of the interface to saturated, non-zero values on the nematic side. Since the two free energy minimum states are degenerate in the bulk, the position of the interface is arbitrary and can be fixed, for concreteness, at $z = 0$ in the infinite system. However, there are subtleties. Provided all components of $Q$ vary substantially only in the neighbourhood of the interface, the interface can be located through several, largely equivalent criteria. However, if variations of $Q$ are not confined to a region proximate to the interface but depend on the system size $L$ irrespective of how large $L$ is, the very isolation of an interface from the bulk is ill-defined. As indicated earlier, it is this situation which obtains in the case of oblique anchoring and the $L \to \infty$ limit must be taken with care.

The central results of this paper are the following: A numerical minimization of the GLdG free energy which imposes a specific oblique anchoring condition on the system deep into the
FIG. 1: The interface geometry and the coordinate system used in this paper. Note that the nematic director makes an angle $\theta$ with respect to the $z-$ axis direction. This angle is fixed at infinity to $\theta = \theta_e$. It can be chosen to vary between $\theta_e = 0$ (homoeotropic anchoring at infinity) and $\theta_e = 90^\circ$ (planar anchoring at infinity). The isotropic phase is favoured, through boundary conditions, as $z \to -\infty$, whereas the nematic phase is favoured for $z \to \infty$. The plane of the interface is the $x-y$ plane, shown by ABCD in the figure, whereas the director is confined to the EFGH plane as shown. The origin is denoted by O.

nematic while fixing the interface location at the origin shows that the elements of $Q$ vary with space even far away from the interface, albeit slowly. Only in the limit of homoeotropic or planar anchoring is the variation of $Q$ confined to a finite region. This variation in the case of oblique anchoring can, however, be split into hydrodynamic and non-hydrodynamic components. Generically, the variation of the non-hydrodynamic components, such as the magnitudes of $S$ and $T$, are confined to a finite region, independent of the system size $L$, if
$L$ is large enough. However, the orientation of the nematic director varies in space: if the asymptotic value of the nematic order parameter at $L$ represents uniaxial ordering along an oblique axis, the director orientation interpolates linearly between either a 90° value preferred at the location of the interface (planar anchoring) or a 0° value (homeotropic anchoring), and the value imposed by the boundary condition at $L$. Whether planar or a homeotropic anchoring is preferred at the interface depends on the sign of the second of the elastic coefficients in the GLdG expansion, the $L_2$ term, as initially shown by de Gennes.

Our results are consistent with the qualitative observations of PWS, but provide a detailed quantitative analysis in the case of oblique anchoring. We scale angle profiles computed for different values of the system size $L$ onto a universal curve, indicating a linear profile. In the limit that $L \to \infty$, the slope with which the phase varies vanishes as $1/L$, so that the total energy cost for elastic distortions of the nematic field $\sim \int (\nabla \theta)^2 dz \sim L(\Delta \theta)^2/L^2 \sim 1/L$, thus vanishing in the thermodynamic limit. Thus, the isotropic-nematic interface with an oblique anchoring constraint imposed on the nematic side can be regarded as being marginally stable, as opposed to unstable, provided the thermodynamic limit is taken with care. We demonstrate that suitably chosen, flexible variational choices for the uniaxial and biaxial profiles can capture the variation of components of the $Q$ tensor as a function of space. These variational profiles are obtained by generalizing results from a calculation of biaxial and uniaxial order parameter profiles in the planar case. These profiles are benchmarked against numerical calculations.

The outline of this paper is the following. In Section II, we briefly review aspects of the Landau-Ginzburg-de Gennes transition which will be required in our analysis and obtain the equations representing the variational minimum of the GLdG free energy, in a basis adapted to the symmetry of the problem. Section III describes solutions to these equations, as appropriate to the cases of planar and homeotropic anchoring. The classic tanh profile obtained by de Gennes is an exact representation of the interface in the limit of homeotropic anchoring as well as when the $L_2$ elastic constant vanishes, in which case the interface is stable for any anchoring condition. In Section IV we present our numerical approach to the problem of interface structure, showing how numerically exact profiles for the variation of $S$, $T$ and $\theta$ can be obtained within the framework of a minimization of the full GLdG free energy, subject only to the condition that an interface is forced into the system.

In Section V we describe our variational approach to this problem, motivating the choice
of a three-parameter variational ansatz inspired by the approximate solution due to Popa-Nita, Sluckin and Wheeler. We show that this variational ansatz captures the features of the solution in both the extreme cases of planar and homoeotropic anchoring, and is flexible enough to describe the intermediate regime as well. In Section VI, we describe our methods of minimization for the variational problem and our results for $L_2 > 0$ and $L_2 < 0$. We describe how our numerical and variational calculations can be used to provide an accurate picture of the interface with an oblique anchoring condition In Section VII we present asymptotic results for the variation of $S, T$ and $\theta$ close to the bulk nematic state. Section VIII contains our conclusions.

II. THE GINZBURG-LANDAU-DE GENNES APPROACH TO THE ISOTROPIC-NEMATIC TRANSITION

The Ginzburg-Landau-de Gennes free energy functional $F = F_h + F_{el}$ is obtained from a local expansion in powers of rotationally invariant combinations of the order parameter $Q(x, t)$,

$$F_h[Q] = \frac{1}{2}ATrQ^2 + \frac{1}{3}BTrQ^3 + \frac{1}{4}C(TrQ^2)^2 + E'(TrQ^3)^2 \ldots,$$

The restriction to the terms shown above are sufficient to yield a first-order transition between isotropic and nematic phases as well as a stable biaxial phase, obtained when $E' \neq 0$.

To this local free energy, non-local terms arising from rotationally invariant combinations of gradients of the order parameter must be added. The choice of the following two lowest-order gradient terms is common:

$$F_{el}[\partial Q] = \frac{1}{2}L_1(\partial_\alpha Q_{\beta\gamma})(\partial_\alpha Q_{\beta\gamma}) + \frac{1}{2}L_2(\partial_\alpha Q_{\alpha\beta})(\partial_\gamma Q_{\beta\gamma}),$$

where $\alpha, \beta, \gamma$ denote the Cartesian directions in the local frame, and $L_1$ and $L_2$ represent the elastic cost for distortions in $Q$. The fact that there are only two terms which appear to this order implies that only two of the three Frank constants are independent. The limit in which $L_2 = 0$, or of zero elastic anisotropy corresponds to the case in which all Frank constants are equal. The relationship between $L_1$ and $L_2$ and the Frank constants $K_1, K_2$ and $K_3$ are the following: $K_1 = K_2 = 9/4(2L_1 + L_2)S^2$ and $K_3 = 9/2L_1S^2[1, 4]$. Note that
\( \kappa = L_2/L_1 \) negative is allowed, although \( \kappa < 1.5 \) must be satisfied to ensure positivity of the elastic constants.

In the free energy density of Eq. 2, \( A = A_0(1-T/T^*) \), where \( T^* \) denotes the supercooling transition temperature. From the inequality \( \frac{1}{7}(Tr\mathbf{Q}^2)^3 \geq (Tr\mathbf{Q}^3)^2 \), higher powers of \( Tr\mathbf{Q}^3 \) can be excluded for the description of the uniaxial phase. Thus the uniaxial case is described by \( E' = 0 \) whereas \( E' \neq 0 \) for the biaxial phase. We will assume that \( E' = 0 \), thus ensuring that the stable ordered phase is the uniaxial nematic. For nematic rod-like molecules \( B < 0 \) whereas for disc-like molecules, \( B > 0 \); for concreteness, we will assume \( B < 0 \) here. The quantity \( C \) must be positive to ensure stability and boundedness of the free energy in both the isotropic and nematic phases.

The first order isotropic to uniaxial nematic transition at the critical value \( S = S_c \) is thus obtained from,

\[
A = \frac{3}{4}CS_c^2 \\
B = -\frac{9}{2}CS_c.
\]

We choose \( B = -0.5, C = 2.67 \) and \( A = B^2/27C \), thus enforcing phase coexistence between an isotropic and uniaxial nematic phase [4].

The interface is taken to be flat and infinitely extended in the \( x-y \) plane. The spatial variation of the order parameter only occurs along the \( z \) direction [8]. We scale \( Q_{\alpha\beta} \rightarrow Q_{\alpha\beta}/S_c \) where \( S_c = -\frac{2B}{9C} \), \( \mathcal{F} \rightarrow \frac{16}{9C}S_c \mathcal{F} \), and measure lengths in units of \( l_c = \sqrt{54C(L_1 + 2L_2/3)/B^2} \).

A. The Ginzburg-Landau-de Gennes Equations

The director \( \mathbf{n} \), sub-director \( \mathbf{l} \) and their joint normal \( \mathbf{m} \) together define a frame. We define \( z \) as the direction perpendicular to the interface. The fixed orientation of the nematic axis at \( z \rightarrow \infty \) can be used to define a plane, the \( xz \) plane. From symmetry, and following the arguments of Sen and Sullivan, the nematic director must always remain in this plane [8]. Thus, the spatial dependence of the frame orientation can only come from the variation of a single tilt angle \( \theta \), which is measured between the \( z \) axis and \( \mathbf{n} \), as shown in Fig. I.

Since we assume a flat interface, the components of \( \mathbf{Q} \) are functions only of \( z \). The tensor
Q in the local frame defined by the principal axes, is diagonal and given by

\[
Q = \begin{pmatrix}
-(S + T)/2 & 0 & 0 \\
0 & -(S - T)/2 & 0 \\
0 & 0 & S
\end{pmatrix}
\]  

(6)

Transforming to the space-fixed frame (the laboratory frame), by rotation through the appropriate angle \( \theta \) yields

\[
Q_\theta = \begin{pmatrix}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-\sin \theta & 0 & \cos \theta
\end{pmatrix}
\begin{pmatrix}
-(S + T)/2 & 0 & 0 \\
0 & -(S - T)/2 & 0 \\
0 & 0 & S
\end{pmatrix}
\begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{pmatrix}
\]  

(7)

Thus, \( Q_\theta \) takes the form

\[
Q_\theta = \begin{pmatrix}
-\frac{1}{2}(S + T) \cos^2 \theta + S \sin^2 \theta & 0 & -\frac{1}{2}(3S + T) \sin 2\theta \\
0 & -(S - T)/2 & 0 \\
-\frac{1}{4}(3S + T) \sin 2\theta & 0 & -\frac{1}{2}(S + T) \sin^2 \theta + S \cos^2 \theta
\end{pmatrix}
\]  

(8)

Inserting this tensor form into the elastic free energy \( F_{\text{el}}[Q] \) yields the elastic contribution to the free energy

\[
F_{g\theta} = \frac{1}{8(3 + 2k)} \left[ (12 + 5k + 3k \cos(2\theta)) \partial_z S^2 + 4k \sin^2(\theta) \partial_z S \partial_z T + 2 \left( 2 + k \sin^2(\theta) \right) \partial_z T^2 \
- \frac{2k \sin(2\theta)(3S + T)}{8(3 + 2k)} \left( \partial_z S - \partial_z T \right) \partial_z \theta + \frac{(2 + k)(3S + T)^2 \partial_z \theta^2}{4(3 + 2k)} \right].
\]  

(9)

Note that this contribution must vanish if \( S, T \) and \( \theta \) are uniform.

The bulk free energy contribution \( F_{h}[Q] \) is unchanged, as a consequence of the fact that the Landau term is constructed from rotationally invariant terms in the order parameter. It then takes the form

\[
F_{h}[Q] = \frac{1}{3} (3S^2 + T^2) - 2(S^3 - ST^2) + \frac{1}{9} (9S^4 + 6S^2T^2 + T^4).
\]  

(10)

The Euler-Lagrange equations minimizing the full free energy \( F \), are obtained from

\[
- \left( \frac{\partial F_{g\theta}}{\partial \theta} \right) + \frac{d}{dz} \left( \frac{\partial F_{g\theta}}{\partial \theta} \right) = 0,
\]  

(11)

where \( \dot{\theta} = d\theta/dz \). This yields

\[
4(2 + k)(3S' + T') \theta' - k \sin(2\theta)(S'' - T'') + 2(2 + k)(3S + T) \theta'' = 0,
\]  

(12)
which can further be simplified as

\[-k \sin(2\theta)(3S + T)(S'' - T'') + (2(2 + k)(3S + T)^2\theta')' = 0, \quad (13)\]

where the primes indicate derivatives with respect to \( z \).

First, note that for \( k = 0 \) (i.e. no elastic anisotropy) the above equation has only the solution \( \theta' = 0 \), implying that \( \theta \) is constant. A similar situation holds for the special \( \theta \) values \( \theta = 0, 90^\circ \), for which again the only solution has \( \theta' = 0 \). Thus, in these special limits, the angle \( \theta \) remains fixed throughout the system. These results are, of course, consistent with the result that planar (\( \theta = 90^\circ \)) and homoeotropic (\( \theta = 0 \)) anchoring conditions yield a well-defined interface. Also, provided elastic anisotropy is absent, one can continue to define a stable interface for an arbitrary \( \theta \), since \( \theta \) sticks to its asymptotic value throughout.

Finally, we note that once \( S \) and \( T \) are saturated, \( S' = T' = S'' = T'' = 0 \), and thus \( \theta' = \) constant, yielding a linear variation of \( \theta \) with \( z \).

For completeness, the full set of Euler-Lagrange equations representing the minimization of the GLdG equations are, in addition to the \( \theta \) equation above

\[- \left( \frac{(k \cos(2\theta) + 6 + 3k)(3S + T)}{6 + 4k} \right) \theta'^2 + \left( \frac{k(4 + 3k + k \cos(2\theta)) \sin(\theta)^2}{4(6 + 7k + 2k^2)} \right) T'' + \left( \frac{96 + 88k + 19k^2 + 12k(2 + k) \cos(2\theta) + k^2 \cos(4\theta)}{16(6 + 7k + 2k^2)} \right) S'' = 2S - 6S^2 + 4S^3 + 2T^2 + 4S \frac{T^2}{3} \quad (14)\]

\[\left( \frac{32 + 24k + 3k^2 - 4k(2 + k) \cos(2\theta) + k^2 \cos(4\theta)}{16(6 + 7k + 2k^2)} \right) T'' + \frac{k(4 + 3k + k \cos(2\theta)) \sin(\theta)^2 S''}{4(6 + 7k + 2k^2)} + \frac{(k \cos(2\theta) - 2 - k)(3S + T)\theta^2}{6 + 4k} = \frac{2}{3}T + 4ST + \frac{4}{9}T^3 + \frac{4}{3}S^2T \quad (15)\]

III. INTERFACE STRUCTURE FOR PLANAR AND HOMOEOTROPIC ANCHORING

This section briefly reviews the methodology for the solution of interfacial structure in the cases of homoeotropic and planar alignment [5]. While the exact solution in the case of homoeotropic alignment, as originally proposed by de Gennes, motivates the canonical
tanh form for the uniaxial order parameter, the more complex situation of planar anchoring requires the simultaneous solution of equations of motion for both $S$ and $T$, in addition to the equation for $\theta$. We discuss how the Popa-Nita, Sluckin and Wheeler solution\cite{6} of the planar case can be generalized, in a variational sense, to the more general problem of an oblique anchoring condition.

A. Homeotropic Alignment

The equation of motion for homeotropic boundary conditions is easily obtained by setting $\theta = 0$, in the defining equations above. This immediately yields,

$$\frac{1}{2} \partial^2_z S = S - 3S^2 + 2S^3 + T^2 + \frac{2ST^2}{3},$$

$$\frac{1}{2(3 + 2k)} \partial^2_z T = \frac{1}{3} T + 2ST + \frac{2T^3}{9} + \frac{2S^2T}{3}. \quad (16) \quad (17)$$

It is easy to see that these equations have the solutions

$$S = \frac{1}{2}(1 + \tanh(\frac{z}{\sqrt{2}})), \quad T = 0; \quad (18)$$

Here the treatment of de Gennes is exact.

B. Planar Alignment

The case of planar alignment follows from setting $\theta = 90^\circ$ in the Euler-Lagrange equations. This then yields the following set of coupled partial differential equations for the $S$ and $T$ order parameters,

$$\frac{(6 + k)}{(3 + 2k)} \partial^2_z S + \frac{k}{(3 + 2k)} \partial^2_z T = 4S - 12S^2 + 8S^3 + 4T^2 + \frac{8ST^2}{3}, \quad (19)$$

$$\frac{k}{(3 + 2k)} \partial^2_z S + \frac{(2 + k)}{(3 + 2k)} \partial^2_z T = \frac{4}{3} T + 8ST + \frac{8T^3}{9} + \frac{8S^2T}{3}. \quad (20)$$

In the zeroth order approximation we drop terms in $T$ as in the solution of the first equation. This then yields $S = \frac{\xi}{2}(1 + \tanh(\frac{z}{\sqrt{2}\xi}))$ where $\xi = \sqrt{\frac{1+k/6}{1+2k/3}}$. Putting this in equation (20), scaling $z$ again with $\sqrt{2}\xi$ and neglecting the nonlinear term, we get the following equation.

$$\partial^2_z T = 2\beta(\tanh^2(z) + 8 \tanh(z) + 9)T$$

$$+ \frac{k}{2+k} \tanh(z)(1 + \tanh(z))(1 - \tanh(z)), \quad (21)$$
with $\beta = \frac{6+k}{3(2+k)}$.

The PSW approximation now consists of dropping the $\partial_z^2 T$ term, yielding the algebraic equation

$$2\beta(\tanh^2(z) + 8 \tanh(z) + 9)T = -\frac{k}{2+k} \tanh(z)(1 + \tanh(z))(1 - \tanh(z)),$$

which then immediately yields

$$T = -\frac{k}{2\beta(2+k)} \frac{\tanh(z)(1 + \tanh(z))(1 - \tanh(z))}{(\tanh^2(z) + 8 \tanh(z) + 9)}.$$ (23)

We have recently suggested an improvement to these results, motivated by our tests of the self-consistency of the PSW approximations. These tests indicate that the $\partial_z^2 T$ term dropped by PWS should be retained for a more accurate description of the interface. Our analytic results for this case, expressed as a sum over hypergeometric functions, agree well with numerical solutions of the GLdG equations and represent a significant improvement over the PSW solution, particularly in the case of small $\kappa$.

IV. NUMERICAL MINIMIZATION OF THE GINZBURG-LANDAU-DE GENNES FREE ENERGY FOR THE INTERFACE PROBLEM

Our numerical results for the isotropic-nematic interface with an oblique anchoring condition are obtained from a direct minimization of the Ginzburg-Landau-de Gennes functional, with boundary conditions which ensure the presence of the interface as well as impose the required anchoring condition on the $\theta$ field. Our numerical methodology is the following: Defining a system size $L$, we discretize the one-dimensional $(z)$ coordinate into $N$ points, defining $\delta = L/N$. We use, typically, $N = 1001$. The values of the fields $S$, $T$ and $\theta$ at each of these points is varied so as to minimize the combined integrals of Eq. 9 and Eq. 10.

To do this, we perform a straightforward evaluation of the integral using the trapezoidal rule, replacing derivative terms in the integrand by the finite difference approximants. Thus, the gradient term $dS/dz \simeq [S(i+1) - S(i)]/\delta$. We have also used a variable discretization in some of our calculations, to assess the accuracy of our results, sampling with closely spaced points in the vicinity of the interface where the variation of $S$ and $T$ is largest. We impose boundary conditions on $S$, $T$ and $\theta$, by fixing the values at the two extreme boundaries to their values in the isotropic ($S = 0, T = 0$) limit, with $\theta$ arbitrary, and in the nematic limit ($S = 1, T = 0, \theta = \theta_c$).
FIG. 2: [Color online] Profiles of the biaxial ($T$) (main figure) and uniaxial ($S$) order (inset) parameter as a function of the coordinate $z$ across the interface, for planar anchoring and $\kappa = 4$ as obtained from a direct numerical minimization of the LGdG functional (solid line). The results obtained from an spectral collocation method are shown as points.

The location of the interface is fixed at the centre, by imposing $S = 1/2$ at the central site. In principle, in a system of finite size $L$, our methods yield a constrained minimum for the following reason: The elastic energy on the nematic side is minimized by allowing the nematic region to expand as far as possible, effectively forcing the interface to invade the isotropic side. However, as discussed above, in the thermodynamic limit $L \to \infty$, this elastic energy cost reduces as $1/L$, vanishing in the thermodynamic limit where a stable interface is obtained. Alternatively, one can think of this in terms of adding a localized pinning potential with strength vanishing as $L \to \infty$, which serves only to stabilize the location of the interface.

This relatively simple approach yields results of very high quality, as we have checked by a direct comparison to exact results for the planar anchoring case as well as to numerical
calculations using spectral methods in the case of planar anchoring. We have used the minimization routines (NMinimize) in Mathematica to find the stationary values of \( S, T \) and \( \theta \) which minimize the free energy subject to the applied boundary conditions. This routine selects the most appropriate methodology from a variety of minimization techniques available, iterating till an accuracy between successive iterations of 1 part in \( 10^8 \) is obtained.

As a test of the quality of the minimization methodology which will be used in this paper, we show in Fig. 2, profiles of the biaxial \((T)\) (main figure) and uniaxial \((S)\) order (inset) parameter as a function of the coordinate \( z \) across the interface, as computed by the numerical spectral methodology of Ref. \[22\] and the minimization technique described above, for the case of planar anchoring i.e. \( \theta_e = 90^\circ \), with \( \kappa = 4 \). Results obtained from the numerical minimization of the LGdG functional are shown as the solid line whereas results from the spectral collocation scheme of Ref. \[22\] are shown as points. These coincide to high accuracy.

V. VARIATIONAL METHOD

Clearly, the solution of the full set of equations for \( S, T \) and \( \theta \) given above is a formidable problem. Our approach to this problem therefore proceeds through the construction of simple, physically motivated variational choices for \( \theta(z), S(z) \) and \( T(z) \). This choice is made keeping in mind that requirement that the results should be consistent with computations in the simpler \( \theta = 0, 90^\circ \) limits, where the angular variation is absent and the de Gennes solution and the PSW solution are obtained, respectively.

Our approach begins by assuming a profile of the form

\[
S = \frac{1}{2}(1 + \tanh(az)) \quad \text{and} \quad T = -b\tanh(cz)\frac{(1 + \tanh(cz))(1 - \tanh(cz))}{\tanh^2(cz) + 8\tanh(cz) + 9},
\]

(24)

together with the assumption that the theta variation can be fitted to a simply parametrizable function. We have examined a variety of such functions for the case of planar anchoring, including (a) \( \theta = 90^\circ - \frac{\psi}{2}z \) for \( z > 0 \), \( 90^\circ \) for \( z < 0 \), (b) \( \theta = 90^\circ - \frac{\psi}{2}(1 + \tanh(a_1z)) \) which implies that at \( z = \infty \), \( \theta = 90^\circ - \psi \) and at \( z = -\infty \), \( \theta = 90^\circ \), (c) \( \theta = 90^\circ - \frac{\psi}{2}(1 + \tanh(a_1z)) \) which implies that at \( z = \infty \), \( \theta = 90^\circ - \psi \) and at \( z = -\infty \), \( \theta = 90^\circ \), (d) \( \theta = \frac{\psi}{2}(1 + \tanh(a_1z)) \) (e) \( \theta = \frac{\psi}{2L}z + \psi/2 \) and (f) \( \theta = p + \frac{\psi}{2}(1 + \tanh(a_1z)). \)
Our best results are obtained with the variational form

$$\theta = p + \psi \frac{z}{L}$$

subject to a constraint $p + \psi = \theta_L$ where $\theta_L$ is the value of angle at $L$, the system size. It will be our intention to take the $L \to \infty$ limit later.

Note that the choice $p = 90^\circ, \psi = 0, a = 1, b = \frac{k}{2(2+4)}$ recovers the profile of PSW for the planar case. The parameter values $\psi = 0, b = 0$ generate the de Gennes solution. Thus, the two extreme limits of the variation of the anchoring angle can be obtained with the appropriate choice of parameter values in the variational form chosen above. These can be simply generalized to the case of homoeotropic anchoring.

VI. NUMERICAL METHODOLOGY FOR THE VARIATIONAL SOLUTION

These variational ansätze for $S$ and $T$ are inserted into the form for the free energy, which is then minimized with respect to the parameters $a, b, c,$ and $p$. This minimization is carried out using Mathematica. We use the ”Nelder-Mead” method for the minimization of a function of $n$ variables. This is a direct search method which uses an initial choice of $n + 1$ vectors which form the vertices of a polytope in $n$-dimensions and a methodology for changing the vertices of this polytope iteratively. The process is assumed to have converged if the difference between the best function values in the new and old polytope, as well as the distance between the new best point and the old best point, are less than preset values, typically of the order of $10^{-10}$.

To eliminate problems arising from an incorrect choice of initial values, we have computed the minima for about 100 separate initial conditions and chosen the parameter values corresponding to the least value of the free energy from these. Our results for the minimization have been crosschecked using the differential evolution method, a simple stochastic function minimizer.

A. Results from the Numerical and Variational Minimization: $\kappa > 0$

In Fig. 3, we show profiles of the biaxial ($T$) and uniaxial ($S$) order parameter as a function of the coordinate $z$ across the interface. These are computed by direct numerical
minimization of the LGdG functional, via the methodology described in the previous section. We allowed $\theta$ on the isotropic side to vary, finding that the free energy minimum was obtained when $\theta$ was stuck to the value it attained at the location of the interface. This value is somewhat smaller than $90^\circ$ for small system sizes but asymptotes to this value as $L$ goes to infinity.

We show the $T$ profile in the main sub-figure for systems of size $L = 50, 1290$ and parameter values (a) $\kappa = 1, \theta_e = 30$ (b) $\kappa = 8, \theta_e = 30$, (c) $\kappa = 1, \theta_e = 60$ and (d) $\kappa = 8, \theta_e = 60$. N and I in the figure refer to nematic and isotropic respectively. The insets to each of (a), (b), (c) and (d) show the corresponding profiles for $S$.

We note that for larger anchoring angles, the $T$ profile converges faster as a function of system size than for smaller angles; contrast the behavior for $\theta_e = 30^\circ$ and $\theta_e = 60^\circ$ in the figure. The profiles are qualitatively similar to profiles obtained for the $\theta_e = 90^\circ$ degree, and asymptotically match this profile as $L \to \infty$.

In the inset to Fig. 4, we show the profile of $\theta$, the angle describing the orientation of the local director field as a function of $z$ across the interface, as obtained from our numerical minimization. We show data for systems of size $L = 125, 258, 516$ and 1290, and for parameter values (a) $\kappa = 1, \theta_e = 30$ (b) $\kappa = 8, \theta_e = 30$, (c) $\kappa = 1, \theta_e = 60$ and (d) $\kappa = 8, \theta_e = 60$. The main figure, in each case, plots the same data as a function of the scaled coordinate $z/L$ on the $x$–axis and the quantity $(\theta - \theta_e)/(\theta_{\text{max}} - \theta_e)$ on the $y$–axis, thus normalizing the value to its maximum. This produces high quality collapse of the data, indicating that the angle profile is linear on the nematic side, interpolating linearly between its value at the interface to the anchored value of $\theta_e$ at $z = L$. Also, as the system size is increased, the value at the interface ($z = 0$), approaches $90^\circ$, indicating that anchoring at the interface is always planar in the asymptotic limit.

In Fig. 5 we show the comparison between the computed 3-parameter variational profile for the angle $\theta$ as a function of the coordinate $z$ across the interface, for a system of size $L = 125$, as obtained from a direct numerical minimization of the LGdG functional (solid line) and from the variational calculation described in the text (point). These are shown for parameter values (a) $\kappa = 1, \theta_e = 30$ (b) $\kappa = 8, \theta_e = 30$, (c) $\kappa = 1, \theta_e = 60$ and (d) $\kappa = 8, \theta_e = 60$. The inset labeled (i) in each sub-figure shows the corresponding profile of $S$, whereas the inset labeled (ii) shows the profile of $T$. Note that the variational result coincides with the result obtained from a direct numerical minimization to high accuracy.
FIG. 3: [Color online] Profiles of the biaxial ($T$) and uniaxial ($S$) order parameter as a function of the coordinate $z$ across the interface, computed by direct numerical minimization of the LGdG functional. These are shown in the main figure for systems of size $L = 50, 1290$ and parameter values (a) $\kappa = 1, \theta_e = 30^\circ$ (b) $\kappa = 8, \theta_e = 30^\circ$, (c) $\kappa = 1, \theta_e = 60^\circ$ and (d) $\kappa = 8, \theta_e = 60^\circ$. The insets to each of (a), (b), (c) and (d) show the corresponding profiles for $S$. N and I refer to nematic and isotropic respectively.
FIG. 4: [Color online] Main figure: Scaled profiles of the angle $\theta$ describing the orientation of the local director field as a function of the scaled coordinate $z/L$ across the interface, as obtained from direct numerical minimization of the LGdG functional for systems of size $L = 125, 258, 516$ and 1290. These are shown for parameter values (a) $\kappa = 1, \theta_e = 30^\circ$ (b) $\kappa = 8, \theta_e = 30$, (c) $\kappa = 1, \theta_e = 60$ and (d) $\kappa = 8, \theta_e = 60$. The insets to each of (a), (b), (c) and (d) show the corresponding unscaled profiles for $\theta$. 
As the system size is increased, the value of $\theta$ at the interface approaches 90° within both the variational and the direct numerical minimization approaches.

Fig. 6 shows the variational parameters $a$ (a), $b$ (b) and $c$ (c) as a function of system size $L$, together with the variation of the variational angle $p$ (d), plotted for $\kappa = 1$. These parameters converge to their $L \to \infty$ values corresponding to the case of planar anchoring. In all cases the parameter $p$ converges to the asymptotic value of 90° as the system size is increased, consistent with planar anchoring.

**B. Results from the Numerical and Variational Minimization: $\kappa < 0$**

Stability imposes the requirement that $3+2\kappa > 0$, but does not constrain the sign of $\kappa$ (or, equivalently $L_2$), apart from this requirement. In this section we explore the consequences of a negative value for $L_2$.

We find that, consistent with de Gennes’ prediction, a negative $L_2$ (or $\kappa$) consistent with stability favours *homoeotropic* anchoring at the interface, in contrast to the case of positive $L_2$. Thus, the biaxiality $T$ generically vanishes as $L \to \infty$, whereas $S$ assumes the canonical tanh form obtained by de Gennes. This can be seen from Fig. 7 which shows the variation of $S$ and $T$, for $L = 125$, plotted for $\kappa = -1$. The anchoring at $L$ is set to an oblique angle of 30°. The $S$ and $T$ profiles are consistent with $T = 0$ for homoeotropic anchoring.

The preference for homoeotropic anchoring can be seen from Fig. 8 which shows the director tilt angle scaled to its minimum value for each system size ($L = 125, 258$ and 516, against $z/L$ for $\kappa = -1$, where an asymptotic, oblique anchoring angle of 30° is imposed on the system at $L$. The inset shows the bare angles as a function of $z$ for these different system sizes. The excellent data collapse indicates that angle profiles in the case of $L_2 < 0$ scale in the same way as the $L_2 > 0$ case, except that homoeotropic anchoring is favoured in this case.

Finally, in Fig. 9 we show, in the main figure, the profile of $T$, the biaxial order parameter, for $\kappa = -1$, in the two extreme cases of planar (0°) and homoeotropic (90°) anchoring, with $L = 50$. Importantly, the profile of $T$ is *inverted* with respect to profiles obtained for $\kappa > 0$, with the minimum appearing on the isotropic side of the interface rather than the nematic side, as earlier. The profile of $S$ is consistent with a tanh form. While the profile of $T$ is non-zero for planar anchoring, biaxiality vanishes for the homoeotropic anchoring case.
FIG. 5: [Color online] Main figure: Profiles of the angle $\theta$ describing the orientation of the local director field as a function of the coordinate $z$ across the interface for a system of size $L = 125$, as obtained from a direct numerical minimization of the LGdG functional (solid line) and from the variational calculation described in the text (point). These are shown for parameter values (a) $\kappa = 1, \theta_e = 30^\circ$ (b) $\kappa = 8, \theta_e = 30^\circ$, (c) $\kappa = 1, \theta_e = 60^\circ$ and (d) $\kappa = 8, \theta_e = 60^\circ$. The inset labeled (i) in each sub-figure shows the corresponding profile of $S$, whereas the inset labeled (ii) shows the profile of $T$. N and I refer to nematic and isotropic, respectively.
FIG. 6: [Color online] The variation of the variational parameters $a$ (a), $b$ (b) and $c$ (c) with system size $L$, together with the variation of the variational angle $p$ (d), plotted for $\kappa = 1$. Note that these parameters quickly converge to their $L \to \infty$ values corresponding to the case of planar anchoring. In all cases the parameter $p$ appears to converge to the asymptotic value of $90^\circ$ as the system size is increased.
FIG. 7: [Color online] The variation of the $S$ and $T$, for system size $L = 125$, plotted for $\kappa = -1$, with an oblique anchoring angle of 30°. Our results are consistent with $T = 0$ for homoeotropic anchoring.

These results are consistent with the general trends observed in the case of $\kappa > 0$, with the difference that homoeotropic, rather than planar, anchoring is preferred once $\kappa$ turns negative.

VII. ASYMPTOTIC SOLUTION

We can use our ansatz for $S$ and $T$ to check the self-consistency of our conjectured behaviour for $\theta$. Our chosen forms imply $S = 1 - e^{-2az}$ and $T = -be^{-2az}$ deep into the nematic phase, as $z \to \infty$. Then $S' = 2ae^{-2az}$, $T' = 2abe^{-2az}$ and $S'' = -4a^2e^{-2az}$, $T'' = -4a^2be^{-2az}$. Inserting these into the equation for $\theta$ as below,

$$4(2 + k)(3S' + T') \theta' - k \sin(2\theta)(S'' - T'') + 2(2 + k)(3S + T)\theta'' = 0,$$

(26)
FIG. 8: [Color online] Plot of the angle scaled to its minimum value for each system size ($L = 125, 258$ and 516, against $z/L$ for $\kappa = -1$ and an asymptotic, oblique anchoring angle of $30^\circ$. The inset shows the bare angles as a function of $z$ for these different system sizes. Note that the excellent data collapse indicates that angle profiles in the case of $L_2 < 0$ scale in the same way as the $L_2 > 0$ case, with a homoeotropic anchoring being favoured at the interface.

we get

$$8(2 + k)(3 + b)ae^{-2az}\theta' + k\sin(2\theta)(1 - b)a^2e^{-2az} + 6(2 + k)\theta'' = 0. \quad (27)$$

As $z \to \infty$, this equation reduces to $\theta'' = 0$. Thus, $\theta$ should have a linear profile in this asymptotic limit, taking the form

$$\theta = p + \psi \frac{z}{L}. \quad (28)$$

We can also compute corrections to this profile for $z \to \infty^-$. Let us now expand about the $z = \infty$ limit, in which case $\theta'' = 0$. Thus,

$$\frac{\theta'}{\sin(2\theta)} = -ka(1 - b) = \frac{2(2 + k)(3 + b)}{2(2 + k)(3 + b)}. \quad (29)$$

Integrating the left-hand side of this equation, we obtain

$$\frac{1}{2} \ln \tan(\theta) - \ln C = \frac{-ka(1 - b)z}{2(2 + k)(3 + b)}, \quad (30)$$
FIG. 9: [Color online] Main Figure: Profile of $T$, the biaxial order parameter, for $\kappa = -1$, in the two extreme cases of planar ($0^\circ$) and homoeotropic ($90^\circ$) anchoring. Note that the profile of $T$ is inverted with respect to profiles obtained for $\kappa > 0$, with the minimum appearing on the isotropic side of the interface. INset: The profile of $S$, consistent with a tanh form. Data are computed for $L = 50$. While the profile of $T$ is non-zero for planar anchoring, biaxiality vanishes for the homoeotropic anchoring case.

which has a solution $\theta = \tan^{-1}[Ce^{-\frac{k\mu(1-b)z}{(2+k)(3+b)}}]$. It can be seen that this will vanish as $z$ goes to $\infty$ and is, in effect, negligible apart from a region close to the interface, at $z = 0$.

VIII. SUMMARY AND CONCLUSIONS

In this paper, we have presented our results for the problem of the isotropic-nematic interface within Ginzburg-Landau-de Gennes theory, for the case in which an oblique anchoring condition is imposed on the system asymptotically on the nematic side. In this case, we find that nematic elasticity dictates that the nematic orientation smoothly interpolates between a value of $90^\circ$ at the interface (planar anchoring) to the anchored value at the boundary on the nematic side when $\kappa > 0$. Thus, the preferred value of the anchoring angle at the inter-
face is 90° in this case. The case $\kappa < 0$ with $\kappa$ satisfying the stability requirement $\kappa > -1.5$ leads to stable homeotropic anchoring at the interface, as predicted by de Gennes.

We have used simple variationally based descriptions of the structure of the interface, with our methods capturing essential features of interface structure, both qualitatively and quantitatively, for the case of oblique anchoring. Our methods access the non-trivial structure of biaxiality at the interface, including the large tail towards the isotropic side and the change in the sign of the biaxial order parameter across the interface. Our approach also captures the inversion of the profile of biaxiality as $\kappa$ crosses zero.

The results presented here are broadly consistent with results from density functional approaches, molecular simulations and approaches based on the Onsager functional, but necessitate fewer approximations, truncations or assumptions about specific model systems. Thus, coarse-grained approaches based on the Ginzburg-Landau-de Gennes functional provide a powerful methodology for understanding generic features of the isotropic-nematic interface.

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