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Landau—de Gennes theory of wetting and orientational transitions at a nematic-liquid—substrate interface

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The surface phases of a nematic liquid in the presence of a smooth substrate are studied using Landau—de Gennes theory. The alignment of the nematic director is restricted to be either parallel or perpendicular to the substrate, although methods of treating more general structures are indicated. We describe extensions and a synthesis of earlier studies which obtained analytic solutions of the theory in certain limits, including surface-induced biaxiality, to determine the domains of wetting by planar and homeotropic nematic films as well as by the isotropic phase, as a function of surface-interaction parameters. The relation of wetting to orientational transitions in the surface-induced bulk alignment is discussed. The "parabolic approximation" recently introduced in related contexts is used to obtain solutions of the theory in more general circumstances where exact analytic solutions are precluded. It is found that, for realistic values of the ratio of model elastic constants, complete wetting by planar nematic films exhibits "reentrant" behavior and does not occur for arbitrarily strong substrate potentials. We argue that this outcome is not an artifact of the parabolic approximation, despite several deficiencies of the method. The relevance to experimental studies of nematic-liquid—substrate interfaces is described.

I. INTRODUCTION

Liquid crystals are prime examples of systems which exhibit what may be called "surface-induced ordering."[1] There have been several observations of enhanced stability of nematic[2] and smectic[3] phases near interfaces, as evidenced by their relative adsorption or wetting behavior.[4,5] Nonetheless, even in the simpler, prototypical case of a nematic liquid crystal, fundamental questions concerning the interfacial-ordering process remain to be answered.[5] The main difficulties facing theoretical analyses stem from the fact that the interfacial structure of nematic liquid crystals generally must be characterized by multiple spatially varying order parameters, even when a single-order-parameter description suffices in bulk.

As stressed in some recent works,[4,5] orientational ordering of uniaxial molecules at an interface along a "director" axis $\hat{\mathbf{n}}$ which does not coincide with the interface normal is always associated with broken biaxial symmetry. The director itself may also vary through the interface.[6] Biaxiality plays an essential, if not often recognized, role in distinguishing between various types of interfacial structure, for example, between "random planar" and "homogeneous" (planar aligned) states of a nematic film adsorbed from the bulk isotopic phase onto a substrate which favors parallel molecular orientation. Recent observations[7,8] of homogeneous nematic films on substrates which have *not* been treated (e.g., by "rubbing" or by preadsorption of a suitable material) so as to favor a specific direction of alignment in the surface plane suggest the importance of spontaneous symmetry breaking as opposed to "topographical" mechanisms[9] for the development of surface order.

There have been several previous studies of nematic-liquid—substrate interfaces using the well-known Landau—de Gennes theory.[10-13] With the exception of the most recent work by Sluckin and Poniewierski,[13] all of these ignored biaxiality and hence, in effect, were limited to describing orientational ordering along the interface normal, i.e., in "homeotropic" alignment. The solutions of the theory in that case yield adsorption and wetting behavior typical of systems with Ising-like symmetry.[14] The work in Ref. 13 goes a significant step further by accounting for biaxiality and spontaneous ordering in *planar* nematic films. This was achieved by analytic solution of the Landau—de Gennes theory in the singular limit that the elastic constant L_1 of that theory vanishes.

The present article describes generalizations of the above work in several directions. An outline of the main topics treated is as follows. Section II begins by summarizing the Landau—de Gennes[15,16] formalism for a nematic fluid near a smooth substrate, accounting for biaxiality and arbitrary director alignment. An accompanying appendix provides details on the origin of substrate-dependent terms entering the theory. Some preliminary aspects concerning the spatial variation of the director and how it is influenced by both the elastic constants and parameters of the model fluid-substrate interaction are discussed. We also point out the relevance of the identity of the bulk Landau—de Gennes free energy with that obtained for the three-state Potts model.[17]

The remainder of the paper examines the solutions of the theory when the alignment is restricted to be either planar or homeotropic. (In several situations involving wetting-layer growth, such solutions are probably unstable relative to ones exhibiting director distortion, but detailed treatment of the latter is deferred to future work.) Section III discusses some further consequences of the one-order-parameter limits where analytic solutions can be achieved. We point out the occurrence in the Sluckin-Poniewierski limit[13] $L_1=0$ of additional types of behavior beyond those explicitly described in Ref. 13, viz., partial wetting by a biaxial nematic film at bulk nematic-isotropic coexistence, and continuous wetting transitions.[14] The former state probably characterizes the homogeneous films observed[7,8] on tangentially isotropic substrates. We also discuss the solutions of the model in the regime of wetting by the isotropic phase, and a closely connected orientational transition between planar and homeotropic alignment.

Section IV describes the application of an approximate method recently developed in related contexts[18,19] to obtain analytic solutions of the theory in cases of planar alignment when $L_1 > 0$. A striking result found is that, for what are believed to be experimentally relevant ranges of the elastic constants, there are wide domains in the space of surface parameters where complete wetting by planar nematic films does not occur, no matter how great is the strength of the nematic-liquid—substrate aligning potential. While we cannot rule out that such an outcome is due to the approximate method of solution, or to the neglect of fluctuations inherent in a mean-field approach, an argument supporting the qualitative validity of the results is given in the concluding Sec. V. The absence of any observed cases of complete—as opposed to partial—wetting by biaxial nematic layers on isotropic substrates (noted in Ref. 5), and the analogy to the restricted domain of complete wetting by *solid* films,[20,21] are also consistent with this finding.

II. LANDAU—de GENNES THEORY

A. Summary

We shall begin by summarizing the main constituents of Landau—de Gennes theory for a nematic fluid in the presence of a substrate. (A recent comprehensive review is given in Ref. 5.) Picturing the nematic fluid as composed of uniaxial rodlike molecules with inversion symmetry, we follow custom in taking the basic order parameter to be the tensor

$$\underline{Q}(\mathbf{r}) = \langle \tfrac{1}{2}(3\hat{\mathbf{e}}\hat{\mathbf{e}} - \underline{I}) \rangle \;, \tag{2.1}$$

where $\hat{\mathbf{e}}$ is a unit vector along the symmetry axis of a molecule at position $\mathbf{r}$, $\underline{I}$ is the second-rank unit tensor, and the angular brackets denote a thermal average. Due to its traceless, symmetric character, $\underline{Q}$ can always be represented as[22]

$$\underline{Q}(\mathbf{r}) = \frac{\eta}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}} - \underline{I}) + \frac{\sqrt{3}}{2}\mu(\hat{\mathbf{l}}\hat{\mathbf{l}} - \hat{\mathbf{m}}\hat{\mathbf{m}}) \;, \tag{2.2}$$

where the unit vectors $\hat{\mathbf{l}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}$ form a local orthonormal triad. (The arbitrary factor of $\sqrt{3}$ multiplying the second term has been inserted for later convenience.) The direction of maximum orientational ordering will by convention be associated with the director axis $\hat{\mathbf{n}}$. The presence of any spatial nonuniformity in a direction which does not coincide with $\hat{\mathbf{n}}$ breaks the cylindrical symmetry of the average molecular environment, hence we must generally allow $\underline{Q}(\mathbf{r})$ to be biaxial, i.e., $\mu \neq 0$, despite the assumption of uniaxial molecular symmetry.[4-6] Biaxiality arises in *bulk* smectic-*C* (Ref. 23) and cholesteric[24] liquid crystals for entirely the same reason. The tensor $\underline{Q}$ is thus generally specified by five independent variables, namely η, μ, and the direction cosines of its axes relative to the laboratory frame.

We assume that the nematic fluid occupies the semi-infinite region $z \geq 0$ and is in contact with a flat wall representing the substrate at $z = 0$. Neglecting fluctuations, $\underline{Q}$ can be assumed to vary only in the z direction. The Landau—de Gennes theory is then based on minimizing the surface free-energy functional (per unit area),[5,10-13]

$$\sigma = \int_0^\infty dz[f_G(\dot{\underline{Q}}(z)) + f_L(\underline{Q}(z)) - f_L(\underline{Q}_b)] + f_S(\underline{Q}(0)) \;, \tag{2.3}$$

where $\underline{Q}_b \equiv \underline{Q}(z \to \infty)$ is the bulk order-parameter tensor and $\dot{\underline{Q}}(z) \equiv d\underline{Q}(z)/dz$. The conventional symmetry-allowed expressions for the local bulk free-energy density f_L and elastic energy density f_G are

$$f_L(\underline{Q}) = A\,\mathrm{Tr}\underline{Q}^2 - B\,\mathrm{Tr}\underline{Q}^3 + C(\mathrm{Tr}\underline{Q}^2)^2 \;, \tag{2.4}$$

$$f_G(\dot{\underline{Q}}) = \frac{L_1}{2}\mathrm{Tr}\dot{\underline{Q}}^2 + \frac{L_2}{2}\hat{\mathbf{k}}\cdot\dot{\underline{Q}}^2\cdot\hat{\mathbf{k}} \;, \tag{2.5}$$

where Tr denotes the trace operation and $\hat{\mathbf{k}}$ is a unit vector along $\hat{\mathbf{z}}$. The phenomenological parameters B, C, L_1, and L_2 are taken to be constants, while A is linearly related to temperature. What we can call the "bare" surface energy f_S will be modeled by an expression, first introduced in Ref. 5, which is the nematic analog of that widely encountered in Landau theory of an Ising-model surface,[25,26]

$$f_S(\underline{Q}) = c_1\hat{\mathbf{k}}\cdot\underline{Q}\cdot\hat{\mathbf{k}} + c_2\mathrm{Tr}\underline{Q}^2 + c_3(\hat{\mathbf{k}}\cdot\underline{Q}\cdot\hat{\mathbf{k}})^2 + c_4\hat{\mathbf{k}}\cdot\underline{Q}^2\cdot\hat{\mathbf{k}} \;, \tag{2.6}$$

where c_1—c_4 are constants. This model for f_S assumes that the ordering axis due to the wall has no preferred tangential component (e.g., the substrate does not contain "grooves"), and is the most general expansion of the surface energy to quadratic order in $\underline{Q}$ consistent with that tangentially isotropic symmetry.

In the Appendix, we discuss how one can approximately derive (2.6) from a molecular mean-field theory.[4,27] In that model, as is similar to the case of an Ising-model surface in mean-field approximation,[25,26] the coefficients c_2, c_3, and c_4 of the quadratic terms in f_S arise from modifications of the mean potential between two molecules near the substrate. The coefficient c_1 has contributions both from that effect and from the direct wall-molecule interaction, and is analogous to the "surface magnetic field" in an Ising model. Despite limitations on the validity of (2.6) within a molecular context, as spelled out in the Appendix, one point deserves emphasis. Consistent with the representation of f_G in (2.5) containing at most squared gradients of $\underline{Q}$, we can rule out the occurrence of any terms in f_S depending on normal gradients of $\underline{Q}(0)$, such as have been proposed in some formulations.[28,29]

In the neglect of fluctuations, especially "twist" excitations, we can assume $\hat{\mathbf{n}}$ to be always in a single plane, say the xz plane.[4] The orientation of the triad $\hat{\mathbf{n}}, \hat{\mathbf{l}}, \hat{\mathbf{m}}$ then depends on only a single angle $\psi \equiv \cos^{-1}(\hat{\mathbf{n}}\cdot\hat{\mathbf{k}})$, depicted in

Fig. 1, which may be interpreted as a local tilt angle. Letting ϕ_i, $i=1,2,3$, denote any one of the independent variables η, μ, and ψ, minimization of σ in (2.3) by standard methods leads to the Euler-Lagrange equations,

$$\frac{d}{dz}\left[\frac{\partial f_G}{\partial \dot{\phi}_i}\right]=\frac{\partial}{\partial \phi_i}(f_G+f_L)\,, \tag{2.7}$$

for all $z \geq 0$, where $\dot{\phi}_i \equiv d\phi_i/dz$, and an "initial condition" at the wall

$$\frac{\partial f_G}{\partial \dot{\phi}_i(0)}=\frac{\partial f_S}{\partial \phi_i(0)}\,. \tag{2.8}$$

The variables η and ψ are taken to approach constant values η_b,ψ_b in the uniform bulk phase as $z \to \infty$; when that phase is isotropic, $\eta_b=0$ and ψ_b is irrelevant. The order parameter μ vanishes as $z \to \infty$, reflecting the absence of bulk biaxiality.

B. Remarks on the tilt angle

We draw attention to a few aspects governing the tilt angle ψ. By rotational invariance, the bulk free-energy density f_L defined in (2.4) is independent of ψ. The gradient energy f_G in (2.5) can be found explicitly in terms of $\{\phi_i,\dot{\phi}_i\}$ using (2.2) and the geometry illustrated in Fig. 1. We shall not give the somewhat complicated expression that results [an equivalent but formally simpler expression is in (2.17) below], but rather state the equation which then follows from (2.7) for $\phi_i=\psi$,

$$2\sqrt{3}(2L_1+L_2)\frac{d}{dz}\left[(\sqrt{3}\eta-\mu)^2\frac{d\psi}{dz}\right]=L_2[\sin(2\psi)](\sqrt{3}\eta-\mu)\frac{d^2}{dz^2}(\eta+\sqrt{3}\mu)\,. \tag{2.9}$$

In the special circumstance that $L_2=0$, this equation integrates to $\psi(z)=\text{const}$, on taking account of the "final conditions" in bulk. In that case, ψ is determined by the solution of $\partial f_S/\partial\psi=0$, cf. (2.8), which minimizes f_S. Relations between the L_i and the Frank elastic constants[30,31] and typical experimental[15] as well as theoretical[32] values of the latter, however, suggest that L_2 normally should be positive, with ratio L_2/L_1 in the range 2–4. For nonzero L_2, a constant value of ψ is consistent with (2.9) only when ψ is either 0 or $\pi/2$, which correspond, respectively, to preferred perpendicular (homeotropic) or planar orientation. Previous work[6,16] indicates that these are the most stable solutions of the Landau–de Gennes theory for a free nematic-isotropic interface when L_2 is negative or positive, respectively.

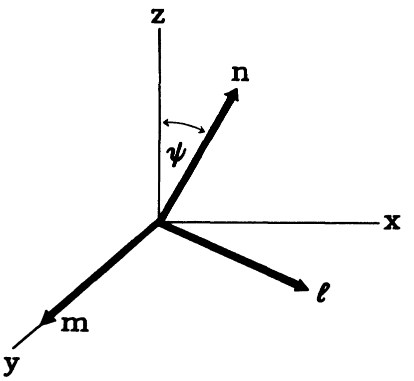

FIG. 1. Orientation of the principal axes of the Q tensor considered in this paper. Both axes $\hat{n}$ and $\hat{l}$ are in the xz plane.

The alignment favored by the bare wall energy f_S (which is all that matters when $L_2=0$) has been discussed previously[5,33] on assuming neglect of biaxiality, but essentially similar results are obtained when the latter is included. On finds that f_S becomes

$$f_S=w_0+w_2\cos^2\psi+w_4\cos^4\psi\,, \tag{2.10a}$$

where, in particular,

$$w_2=\frac{\sqrt{3}}{2}(\sqrt{3}\eta-\mu)[c_1+c_3(\sqrt{3}\mu-\eta)+c_4(\sqrt{3}\mu+\eta)/2]\,, \tag{2.10b}$$

$$w_4=3c_3(\sqrt{3}\eta-\mu)^2/4\,. \tag{2.10c}$$

The order parameters and tilt angle ψ in these expressions are those pertaining to the fluid layer at $z=0$ in contact with the wall. The extrema of (2.10a) are at $\psi=0$, $\pi/2$, and at an *oblique* angle satisfying $\cos^2\psi=-w_2/2w_4$, where the latter is the stable solution when $0<-w_2<2w_4$. If we ignore this possibility (e.g., by decreeing the coefficient c_3 to be negative), then f_S favors either planar or perpendicular alignment according to whether the sum w_2+w_4 is positive or negative, respectively. A transition between these states occurs when (w_2+w_4) vanishes, which is equivalent to the relation

$$c_1=-\tfrac{1}{2}(c_3+c_4)(\eta+\sqrt{3}\mu)\,. \tag{2.11}$$

In general, the most stable alignment must be found by minimizing the *total* free energy σ. Nonetheless, we shall see later that (2.11) closely preserves the relation between the coefficients c_m at a planar-homeotropic transition, provided $(\eta+\sqrt{3}\mu)$ is replaced by a suitable "effective" surface order parameter.

In the remainder of this paper we shall limit consideration to the constant-ψ solutions, either $\psi=0$ or $\psi=\pi/2$, of the Landau–de Gennes theory. We shall point out a number of situations, however, where those solutions are likely to be less stable than ones which admit a spatially varying $\psi(z)$.

C. Transformations of the free energy

Before proceeding, it is convenient to scale out material constants by defining

$$\bar{\eta}=6C\eta/B,\ \ \bar{\mu}=6C\mu/B,\ \ t=24AC/B^2\,. \tag{2.12a}$$

Appropriate reduced distance and energy densities are, respectively, $\bar{z}=z/\xi$ and

$$\begin{aligned}\bar{f}_L&=\left[\frac{24}{B^2}\right]^2 C^3 f_L\,,\\ \bar{f}_G&=\left[\frac{24}{B^2}\right]^2 C^3 f_G\,,\\ \bar{f}_S&=\left[\frac{24}{B^2}\right]^2 C^3 f_S/\xi\,,\\ \bar{\sigma}&=\left[\frac{24}{B^2}\right]^2 C^3 \sigma/\xi\,,\end{aligned}\tag{2.12b}$$

where $\xi=[24C(L_1+2L_2/3)/B^2]^{1/2}$. The coefficients in the wall energy (2.6) will be scaled as $\bar{c}_m=(24C/B^2\xi)c_m$ for $m=2,3,4$, and $\bar{c}_1=(96C^2/B^3\xi)c_1$. Henceforth, it will be understood that such scaling has been carried out, and we shall omit the overbars.

Using the representation of $\underline{Q}$ given in (2.2), we find that the bulk free-energy density f_L becomes

$$f_L=t(\eta^2+\mu^2)-2\eta(\eta^2-3\mu^2)+(\eta^2+\mu^2)^2\,. \tag{2.13}$$

This expression has the same form as the Landau free energy of the three-state Potts model,[17] and is well known to exhibit threefold symmetry in the (η,μ) plane, see Fig. 2. Below the first-order transition occurring when the dimensionless temperature $t=1$, f_L has three symmetrically located global minima at $(\eta,\mu)=(\eta_c,0)$ and $(\eta_c/2,\ \pm\sqrt{3}\eta_c/2)$, where

$$\eta_c=\tfrac{3}{4}(1+\sqrt{1-8t/9})\,. \tag{2.14}$$

These minima or "fixed points" become metastable relative to the isotropic-phase minimum at $(\eta,\mu)=(0,0)$ for $1<t<\frac{9}{8}$, and disappear for $t>\frac{9}{8}$, the superheating limit. The isotropic fixed point is metastable for $0<t<1$, and disappears for $t<0$, the supercooling limit. The degeneracy associated with the nematic fixed points reflects the freedom in choosing any one of the axes $\hat{\mathbf{n}}$, $\hat{\mathbf{l}}$, or $\hat{\mathbf{m}}$ in (2.2) to be "the" director axis, i.e., that axis associated with the maximum component of $\underline{Q}$, and does not indicate the presence of distinct phases. The conventional choice of $\hat{\mathbf{n}}$ as the director puts the physically relevant minimum at $(\eta,\mu)=(\eta_c,0)$. When μ vanishes, (2.13) reduces to the familiar Landau–de Gennes free energy of a bulk uniaxial nematic liquid crystal. Physically equivalent descriptions of the bulk nematic phase are provided along either of the lines $\mu=\pm\sqrt{3}\eta$ in Fig. 2. It follows that although $\mu\neq 0$ along those lines, they do not represent intrinsically biaxial states.

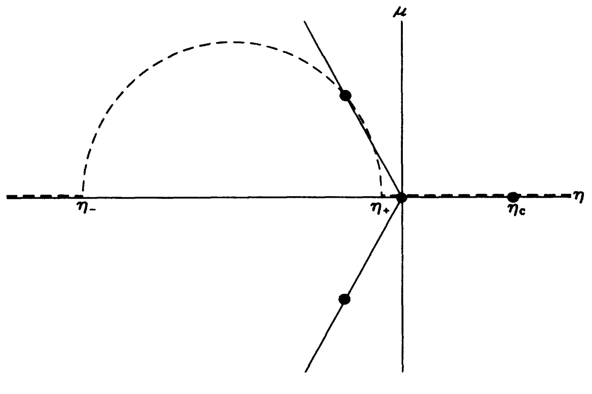

FIG. 2. Fixed points (circles) of the Landau–de Gennes or three-state Potts-model free energy f_L. The dashed curved shows the trajectory $\mu^*(\eta)$ of (3.1).

Now, it turns out to be practicable to reexpress $\underline{Q}$ in terms of its components in a lab-fixed frame. Letting $\hat{\mathbf{i}},\hat{\mathbf{j}},\hat{\mathbf{k}}$ denote unit vectors along the laboratory x,y,z axes, respectively, one finds (see Fig. 1 and note that $\hat{\mathbf{j}}$ coincides with $\hat{\mathbf{m}}$)

$$\underline{Q}=\frac{\eta_s}{2}(3\hat{\mathbf{k}}\hat{\mathbf{k}}-\underline{I})+\frac{\sqrt{3}}{2}\mu_s(\hat{\mathbf{i}}\hat{\mathbf{i}}-\hat{\mathbf{j}}\hat{\mathbf{j}})+\frac{\sqrt{3}}{2}\nu_s(\hat{\mathbf{i}}\hat{\mathbf{k}}+\hat{\mathbf{k}}\hat{\mathbf{i}})\,, \tag{2.15}$$

where the new variables are related to η, μ, and ψ by

$$\begin{aligned}\eta_s&=\eta-\frac{\sqrt{3}}{2}(\sqrt{3}\eta-\mu)\sin^2\psi=\langle\tfrac{1}{2}(3e_z^2-1)\rangle\,,\\ \mu_s&=\mu+\tfrac{1}{2}(\sqrt{3}\eta-\mu)\sin^2\psi=\frac{\sqrt{3}}{2}\langle e_x^2-e_y^2\rangle\,,\\ \nu_s&=\tfrac{1}{2}(\sqrt{3}\eta-\mu)\sin(2\psi)=\sqrt{3}\langle e_xe_z\rangle\,.\end{aligned}\tag{2.16}$$

The second entries on the right-hand side give the molecular interpretation of these variables following from (2.1). The main advantage of this representation is that both the elastic energy f_G and wall energy f_S acquire diagonal forms[23] in terms of η_s, μ_s, and ν_s. Recalling the scaling described above, evaluation of (2.5) and (2.6) with $\underline{Q}$ given by (2.15) yields

$$f_G=\tfrac{1}{2}\dot{\eta}_s^2+\frac{L}{2}\dot{\mu}_s^2+\frac{M}{2}\dot{\nu}_s^2\,, \tag{2.17}$$

$$f_S=c_1\eta_s+c_{2\eta}\eta_s^2+c_{2\mu}\mu_s^2+c_{2\nu}\nu_s^2\,, \tag{2.18}$$

where the reduced elastic constants are

$$L=\frac{L_1}{L_1+2L_2/3},\quad M=\frac{L_1+L_2/2}{L_1+2L_2/3}\,, \tag{2.19}$$

while the renamed surface coefficients are

$$\begin{aligned}c_{2\eta}&=c_2+2(c_3+c_4)/3\,,\\ c_{2\mu}&=c_2\,,\\ c_{2\nu}&=c_2+c_4/2\,.\end{aligned}\tag{2.20}$$

When ψ is restricted to be either 0 or $\pi/2$, (2.16) shows that the order parameter ν_s vanishes identically. In this case, one can verify that the free-energy density f_L is given in terms of the variables η_s and μ_s by the same expression as in (2.13). One notes from (2.16) that η_s and μ_s are identical to η and μ when $\psi=0$, hence the associated bulk nematic fixed point is at $(\eta_s,\mu_s)=(\eta_c,0)$, In contrast, when $\psi=\pi/2$, that fixed point corresponds to $(\eta_s,\mu_s)=(-\eta_c/2,\sqrt{3}\eta_c/2)$. One could alternatively describe the case of $\psi=\pi/2$ using the original variables η and μ, but the elastic energy would then be given by a slightly less-simple expression than that in (2.17), and we shall see that there is some advantage in using different fixed points to represent perpendicular and planar nematics.

For later reference we note from (2.16) that the condition $\mu_s=0$ signifies the absence of ordering along any specific axis parallel to the surface. In this circumstance the alignment is random planar or homeotropic according to whether η_s is negative or positive, respectively.

The Euler-Lagrange equations in (2.7) and (2.8) still hold when $\{\phi\}$ stand for the variables (η_s,μ_s,ν_s). We shall not refer to the original order parameters η and μ, so for notational convenience we shall henceforth drop the subscripts on η_s, μ_s, and ν_s. Neglecting the last of these, we have

$$\ddot{\eta}=\frac{\partial f_L}{\partial \eta}\ , \tag{2.21a}$$

$$L\ddot{\mu}=\frac{\partial f_L}{\partial \mu}\ , \tag{2.21b}$$

for arbitrary z, where $\ddot{\phi}_i \equiv d^2\phi_i/dz^2$, and at $z=0$,

$$\dot{\eta}(0)=c_1+2c_{2\eta}\eta(0)\ , \tag{2.22a}$$

$$L\dot{\mu}(0)=2c_{2\mu}\mu(0)\ . \tag{2.22b}$$

A first integral of (2.21) is

$$f_G(\dot{\eta},\dot{\mu})=f_L(\eta,\mu)-f_L(\eta_b,\mu_b)\equiv\Delta f_L(\eta,\mu)\ , \tag{2.23}$$

where η_b,μ_b are the bulk values of the order parameters, corresponding to the appropriate fixed point in Fig. 2. The solution of these equations is discussed in the remainder of this paper.

III. ANALYTIC MODELS

A *possible* solution of (2.21) and (2.22) when the bulk phase is isotropic ($t\geq 1$) is $\mu=0$ for all z. The ability to realize such a solution is connected to the absence of a constant term in the initial condition (2.22b) analogous to the c_1 term in (2.22a), which in turn reflects the absence of a preferred tangential ordering axis imposed by the substrate. If, at the same time, η is negative, then that solution describes a uniaxial random planar state; however, as will be seen shortly, that state may become less stable than one allowing for biaxiality.

When the bulk phase is nematic ($t\leq 1$), $\mu=0$ is compatible with the final conditions at infinite z only when the alignment in that phase is homeotropic. As remarked earlier, a planar-aligned ($\mu\neq 0$) state would be uniaxial if the order parameters satisfied $\mu=-\sqrt{3}\eta$ for all z. One can easily verify, however, that such a relation is not compatible with both Euler-Lagrange equations in (2.21) except when $L=1$, i.e., $L_2=0$. Even in the latter case, one could not (except by accident) achieve consistency with both initial conditions in (2.22). This proves the necessarily of biaxiality for planar-aligned interfaces.

The one-component model that results when μ is decreed to be zero has been discussed in earlier work.[10–12] The *physically relevant* solutions of that model are also contained in the Sluckin-Poniewierski[13] model, to which we now turn. The latter is obtained by setting $L \propto L_1=0$, in which case (2.21b) simplifies to the algebraic relation $\partial f_L/\partial\mu=0$. If the solution of this equation which minimizes f_L is denoted $\mu^*(\eta)$, we find from (2.13) that

$$\begin{aligned}\mu^*(\eta)&=[(\eta_+-\eta)(\eta-\eta_-)]^{1/2}\quad\text{for } \eta_-<\eta<\eta_+\ ,\\ &=0 \quad\text{otherwise}\end{aligned} \tag{3.1}$$

where

$$\eta_\pm=-\tfrac{3}{2}\left(1\mp\sqrt{1-2t/9}\right)\ . \tag{3.2}$$

The "trajectory" $\mu^*(\eta)$ at a temperature in the range $0<t<\frac{9}{8}$ is indicated in Fig. 2. When this is used in (2.21a), the latter reduces to an effective one-component equation for the variable η. There is a subtle point, however. When $L=0$, the initial condition (2.22b) forces $\mu(0)$ to be zero unless the parameter $c_{2\mu}=c_2$ also vanishes. One might argue on the basis of the model in the Appendix [compare (A8c) and (A8e)] that it is consistent for L_1 and c_2 to vanish simultaneously, but that is not necessarily true in a more general phenomenological model. In the following discussion we shall disregard the initial condition (2.22b); the legitimacy of doing so will be discussed at the end of the section.

The solution of the model is easily obtained using the relation (2.23), which becomes

$$\dot{\eta}=\operatorname{sgn}(\eta_b-\eta)\sqrt{2\Delta f_L(\eta)}\ , \tag{3.3}$$

where $\Delta f_L(\eta)\equiv\Delta f_L(\eta,\mu^*(\eta))$. In the temperature interval $0\leq t\leq\frac{9}{8}$ the latter function exhibits local minima at the bulk fixed points $\eta=-\eta_c/2$, 0, and η_c, where the first and last have equal free energy Δf_L and are absolutely stable for $t<1$, while the minimum at $\eta=0$ is most stable for $t>1$. Taking account of the initial condition (2.22a), this features leads to various possible wetting characteristics on approaching bulk isotropic-nematic coexistence, quite analogous to the behavior of other one-component Landau models and easily discerned by the same type of graphical analysis as applied to those models.[14,25] One difference arises in the present context. When the bulk phase is nematic, and in the explicit absence here of any bulk ordering field or another wall which fixes the alignment of that phase, the latter is not arbitrary but rather must be chosen to minimize the interfacial free energy σ. This leads to the occurrence of an orientational transition in the surface-induced bulk alignment when $\sigma_{W\text{-}N_\parallel}=\sigma_{W\text{-}N_\perp}$, where the subscripts denote the interface between the wall and either bulk planar ($N_\parallel$) or homeotropic ($N_\perp$) nematic phase.

The resulting surface phase behavior at coexistence ($t=1$) as a function of the coefficients c_1 and $c_{2\eta}$ is shown in Fig. 3. The dashed line running through the origin is the locus of (first-order) orientational transitions; the stable bulk alignment is homeotropic below that line and planar above. The upper and lower solid lines in the figure separate domains of complete wetting (CW) by the nematic phase from regions of partial wetting. These lines are light or bold according to whether the associated wetting transition is first-order or second-order, respectively. The second-order lines for wetting by $N_\parallel$ and $N_\perp$ obey $c_1=c_{2\eta}$, $c_{2\eta}>\sqrt{3/2}$ and $c_1=-2c_{2\eta}$, $c_{2\eta}>1/\sqrt{2}$, respectively. The latter was described earlier by Poniewierski and Sluckin,[12] while continuous wetting

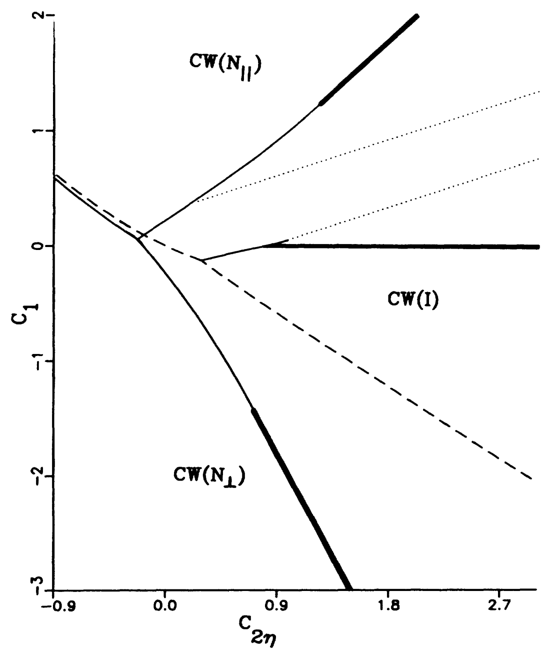

FIG. 3. Surface-phase diagram of the Sluckin-Poniewierski model at bulk N-I coexistence. See explanation in text.

by $N_{\parallel}$ was not discussed by those authors in their later work,[13] which was restricted to $c_{2\eta}=0$. A concomitant generalization of that work is the existence of biaxial partial-wetting $N_{\parallel}$ films when the bulk phase is isotropic. These are stable within the partial-wetting domain above the upper dotted line in Fig. 3, which is a locus of continuous transitions to random planar states. This line is eventually preempted by the first-order $N_{\parallel}$ wetting line.

The first-order wetting lines join at a triple point in the region of negative $c_{2\eta}$, which is believed to ensue under sufficiently strong "surface enhancement" of the pair interactions; cf. the Appendix. For smaller values of $c_{2\eta}$ the separate wetting lines are replaced by a line of direct transitions between planar and homeotropic CW configurations. Notice that the latter lies slightly *below* the line of bulk orientational transitions. One suspects that the features shown in this region, and indeed along the whole $N_{\perp}$ wetting line, will be modified when the constraint of constant alignment is relaxed. For example, the preference for planar alignment at the free nematic-isotropic interface (Sec. II B) should induce a distortion of the director[34] in homeotropic wetting films. For analogous reasons, planar wetting films in the region below the bulk orientational transition line should distort to favor homeotropic alignment near the wall.

The final domain exhibited in Fig. 3 is that of complete wetting by the isotropic (I) phase. This is enveloped by a line of second-order wetting transitions along the $c_1=0$ axis, a brief first-order wetting line extending to negative values of c_1, and the line of orientational transitions. The first- and second-order wetting lines meet at a critical endpoint. The continuation of the first-order line at positive values of c_1 is a locus of symmetry-breaking transitions in the wall-nematic ($N_{\parallel}$) interface, such that the fluid layer immediately adjacent to the wall is uniaxial below that line and biaxial above. This transition is very briefly first order, indicated for clarity by a solid line, and then changes to being continuous at larger values of c_1, indicated by the lower dotted line in the figure.

Some aspects of the isotropic wetting region are suggested by arguments which transcend the Sluckin-Poniewierski model. First, one notes that complete wetting by I when the bulk nematic alignment is homeotropic should always be unstable with respect to complete wetting of bulk $N_{\parallel}$, hence unstable relative to partial isotropic wetting of $N_{\parallel}$ when the latter is favored. This is seen by application of Antonow's rule[35] to the free energy of the wall-nematic interface in the presence of an isotropic wetting layer, once again using the fact that the free energy of the isotropic-nematic interface is minimized by planar alignment. By extension, it follows that complete isotropic wetting of $N_{\parallel}$ could be favored over partial wetting of $N_{\perp}$ for certain parameter ranges, as borne out by the model.

The orientational transition line in this region is very close to being linear, for large $c_{2\eta}$ obeying $c_1 \simeq -0.691 c_{2\eta}$. This should be compared with the relation in (2.11), which under the rescaling described in Sec. II C and with the definitions in (2.20) becomes $c_1=-(c_{2\eta}/2)(\eta+\sqrt{3}\mu)$ when $c_{2\mu}=0$. This evidently fits the model result using an effective value of $\eta+\sqrt{3}\mu$ somewhat larger than its value (equal to unity) at the nematic fixed point.

As usual,[14,25,26] all of the first-order lines in Fig. 3 have associated first-order transitions—either "prewetting" or orientational—which extend to temperatures away from coexistence. Orientational transitions on approaching coexistence have been seen by tilt-angle measurements on SiO substrates,[36] which tend to exhibit complete or nearly complete wetting by the isotropic phase.[36,37] These transitions appear invariably to be *continuous* in nature, and we anticipate that a similar result would be given by the theory on allowing for director distortion. We shall comment some more on this at the end of Sec. IV.

We conclude this section by discussing the effects of nonzero coefficient $c_{2\mu}$ in the initial condition (2.22b). As remarked earlier, that formally leads to the condition $\mu(0)=0$ when $L=0$, which is incompatible with use of the trajectory $\mu^*(\eta)$ of (3.1) when $\eta(0)$ falls between η_+ and η_-. This can be resolved, however, by asymptotic analysis of the theory in the *limit* $L \to 0$. If the solution for the order parameter $\mu(z)$ obtained above with $L=0$ and on disregarding the initial condition (2.22b) is now denoted by $\mu_0(z)$, we find that the correct $\mu(z)$ differs from that result over a region of width $O(L^{1/2})$ and is given in this domain by the expression

$$\mu(z)=\mu_0(z)-2K\mu_0(0)/(K+e^{2\sqrt{2}\mu_0(0)z/L^{1/2}}) + O(L^{1/2}) , \tag{3.4a}$$

where

$$K=[\mu_0(0)-\mu(0)]/[\mu_0(0)+\mu(0)] , \tag{3.4b}$$

and

$$\mu(0)=[\mu_0^2(0)+c_{2\mu}^2/2L]^{1/2}-c_{2\mu}/\sqrt{2L}\ . \tag{3.4c}$$

To the same order in L the function $\eta(z)$ is unchanged under this analysis. When $c_{2\mu}=0$, (3.4) reduces to $\mu(z)=\mu_0(z)$, while the finite deviation $[\mu(z)-\mu_0(z)]$ resulting from *positive* values of $c_{2\mu}$ yields a contribution of $O(L^{1/2})$ to the interfacial free energy σ and hence can be disregarded in the limit $L\to 0$. It is apparent, however, that the limit $L\to 0$ leads to a singularity when $c_{2\mu}<0$, unless this coefficient simultaneously varies proportional to $L^{1/2}$. The interpretation of this singularity is not certain, although the relation of $L\propto L_1$ to the twist elastic constant[31] suggests that it signals an instability with respect to spontaneous surface-induced twist deformations. Similar instabilities at negative values of $c_{2\mu}$ are found when we relax the condition of vanishing L, to be described in the Sec. IV.

IV. PARABOLIC APPROXIMATION

A. Method

We adopt an approach recently applied to several related interface problems described by multicomponent Landau theories.[18,19] While the method has a number of shortcomings and limitations on its range of validity, as will be pointed out, it provides an instructive first step toward elucidating the behavior of multiple-order-parameter nonuniform systems.

In this approach, the function $f_L(\eta,\mu)$ is approximated at each point (η,μ) by $\min[f_I(\eta,\mu),f_N(\eta,\mu)]$, where $f_I(\eta,\mu)$ and $f_N(\eta,\mu)$ are quadratic functions which fit the exact f_L near each of its fixed points.[18,19] (Related ideas have been discussed in Refs. 38 and 39.) Near the isotropic and planar nematic fixed points of Fig. 2 we have from (2.13),

$$f_I(\eta,\mu)=t(\eta^2+\mu^2)\ , \tag{4.1}$$

$$f_N(\eta,\mu)=f_c+\tfrac{1}{2}f_{\eta\eta}(\eta+\eta_c/2)^2+f_{\mu\mu}(\mu-\sqrt{3}\eta_c/2)^2+f_{\eta\mu}(\eta+\eta_c/2)(\mu-\sqrt{3}\eta_c/2)\ , \tag{4.2}$$

where $f_c=f_L(-\eta_c/2,\sqrt{3}\eta_c/2)=f_L(\eta_c,0)$ and $f_{\eta\eta}$, $f_{\mu\mu}$, and $f_{\eta\mu}$ are the appropriate second derivatives of f_L evaluated at the point $(-\eta_c/2,\sqrt{3}\eta_c/2)$. An expansion equivalent to (4.2) also holds near the homeotropic nematic fixed point of Fig. 2. On both physical and mathematical grounds solutions which occur in this region should be uniaxial and thus can be derived exactly, as described in Sec. III. To compare surface free energies in some situations of competing alignment, nonetheless, for consistency we have also applied the "parabolic approximation" to those one-component cases.

Formally, this scheme is restricted to the range of temperatures between the supercooling and superheating limits, $0<t<\frac{9}{8}$, and in practice to temperatures very near coexistence. One can show that the contour defined by $f_I(\eta,\mu)=f_N(\eta,\mu)$, separating domains of the (η,μ) plane in which one or the other quadratic function is smallest, is elliptical about the nematic fixed point for $0<t<1$, hyperbolic for $1<t<\frac{9}{8}$, and parabolic at $t=1$. The last case is shown in Fig. 4.

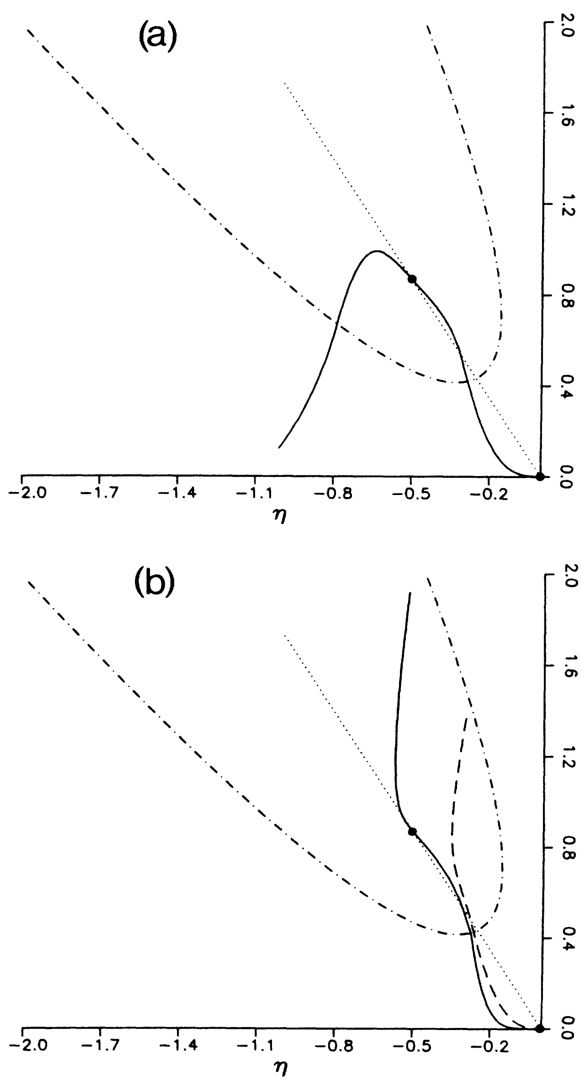

FIG. 4. Selected phase-plane trajectories in parabolic approximation for wetting by the planar nematic phase. The dot-dash curve is the matching line satisfying $f_N(\eta,\mu)=f_I(\eta,\mu)$. (a) A typical reentrant trajectory (solid line), under conditions $L_2/L_1=20$, $c_{2\eta}=4$, $c_{2\mu}=0.5$, $c_1=9.2$. (b) Trajectories near a continuous wetting transition, for parameters $L_2/L_1=10$, $c_{2\eta}=3$, $c_{2\mu}=-0.2$. The dashed curve corresponds to partial wetting, with $c_1=1.2$, while the solid curve describes complete wetting, at $c_1=1.365$.

For concreteness, we shall illustrate the method of solution when the bulk phase is isotropic. As would be appropriate for a case of complete or near complete wetting by the planar nematic liquid let us suppose that the initial point $(\eta(0),\mu(0))$ is located within the "nematic region" on Fig. 4 so that the phase-space trajectory subsequently crosses into the "isotropic region" and thereafter proceeds toward the bulk I fixed point. (More complicated "reentrant" trajectories, cf. Fig. 4(a), can also arise and will be discussed later.) Using (4.1), the solutions of the Euler-Lagrange equations (2.21) in the final, isotropic region must be decaying exponentials for z greater than some distance l,

$$\eta(z)=d_\eta e^{-\sqrt{2t}(z-l)},\quad l\le z<\infty$$
$$\mu(z)=d_\mu e^{-\sqrt{2t/L}(z-l)},\quad l\le z<\infty \tag{4.3}$$

where d_η and d_μ are constants to be determined. Inside the nematic region, the solutions of (2.21) are easily found by diagonalizing the quadratic form in (4.2) (after appropriate rescaling by powers of L), giving the results

$$\eta(z)+\eta_c/2=\Phi_1(z)+\alpha\Phi_2(z),\quad 0\le z<l \tag{4.4a}$$
$$\mu(z)-\sqrt{3}\eta_c/2=[-\alpha\Phi_1(z)+\Phi_2(z)]/\sqrt{L}\,,\quad 0\le z<l$$

where

$$\Phi_i(z)=d_{i1}e^{\lambda_i(z-l)}+d_{i2}e^{-\lambda_i(z-l)},\quad i=1,2 \tag{4.4b}$$

and the four d_{ij} are coefficients to be determined. The decay constants λ_i are related to the second derivatives in (4.2) by

$$2\lambda_i^2=f_{\eta\eta}+f_{\mu\mu}/L\pm[(f_{\eta\eta}-f_{\mu\mu}/L)^2+4f_{\eta\mu}^2/L]^{1/2}\,, \tag{4.4c}$$

while the parameter α is given by

$$\alpha=f_{\eta\mu}/[\sqrt{L}(\lambda_2^2-f_{\eta\eta})]\,. \tag{4.4d}$$

Requiring continuity of $\eta(z)$, $\mu(z)$, and their first derivatives at $z=l$, as well as applying the initial conditions (2.22) to the solutions (4.4) in the nematic region, supplies six linear relations for the unknown parameters. These can be used to express the coefficients d_η, d_μ, and d_{ij} $(i,j=1,2)$ as functions of the matching distance l. A final, nonlinear equation for the latter variable is provided by the condition that the point $(\eta(l),\mu(l))$ lie on the contour where the paraboloids f_I and f_N intersect. Alternatively, one can use the above results for $\eta(z)$ and $\mu(z)$ to evaluate the surface free energy σ given by (2.3), and then minimize the latter with respect to l.[18] The equivalence of these procedures follows from the relation, valid for arbitrary nonequilibrium values of l,

$$\frac{d\sigma_{W\text{-}I}(l)}{dl}=f_N(\eta(l),\mu(l))-f_I(\eta(l),\mu(l))\,, \tag{4.5}$$

where the subscripts on σ designate that it is the free energy of the interface between the wall and bulk isotropic phase. It is clear that l plays a role here similar to that of the usual order parameter for describing wetting transitions, namely the thickness of the wetting layer.[1,26,38,39]

A straightforward calculation gives the intermediate expression

$$\sigma_{W\text{-}I}(l)=\frac{\eta_c}{4}\left[\left[\frac{d\eta}{dz}\right]_{z=l}-\sqrt{3}L\left[\frac{d\mu}{dz}\right]_{z=l}\right]+f_c l$$
$$+\frac{c_1}{2}[\eta(0)-\eta_c/2]-\frac{c_{2\eta}}{2}\eta_c\eta(0)$$
$$+\frac{\sqrt{3}}{2}c_{2\mu}\eta_c\mu(0)\,. \tag{4.6}$$

This is observed to be a linear function of the coefficients d_η, d_μ, and d_{ij}; by substituting for these in terms of l, a final expression for $\sigma_{W\text{-}I}(l)$ is obtained. The latter is generally rather complex and we shall display it only in some special cases [see (4.7) and (4.8) below].

As described later, one very often finds that the absolute minimum of $\sigma_{W\text{-}I}(l)$ occurs at $l=0$. Such a solution is equivalent to the one obtained by having assumed at the outset that the initial point $(\eta(0),\mu(0))$ was located in the isotropic domain of Fig. 4 and that the trajectory never entered the nematic region. The order parameters are then given by (4.3) for all $0\leq z<\infty$, and the relevant coefficients d_η, d_μ trivially obtained by using the initial conditions (2.22). One finds that $d_\mu=0$ (*except* in the circumstance that $2c_{2\mu}+\sqrt{2tL}=0$) and

$$\sigma_{W\text{-}I}(l=0)=\frac{c_1}{2}d_\eta=-\frac{c_1^2}{2(2c_{2\eta}+\sqrt{2t}\,)}\,. \tag{4.7}$$

The vanishing of d_μ, hence of $\mu(z)$, in this case indicates that all trajectories to the bulk isotropic phase which do not begin in (more generally, do not pass through) the region of the nematic fixed point are forced to be uniaxial. A corollary follows from (4.5). Since $f_N>f_I$ whenever $\mu=0$, it ensues that $d\sigma_{W\text{-}I}/dl\mid_{l=0}>0$. This implies that there is always a free-energy barrier between uniaxial (random-planar) and biaxial states at the wall—isotropic-phase interface, hence that any transitions between these states must be first-order. We are uncertain whether or not this is an artifact of the parabolic approximation.[40]

Modification of the above procedure when the bulk phase is the planar nematic, subject to partial or complete wetting by the isotropic phase, is straightforward. We remark only that, in contrast to the preceding case, there is no necessity for $d\sigma_{W\text{-}N_\parallel}/dl\mid_{l=0}$ to be positive.[18] One further case, which is contained in either of the ones above when there is complete wetting at coexistence, is that of the free isotropic-nematic interface. The matching distance l for the latter by itself is arbitrary and can be set to zero,[18,19] where the bulk nematic (isotropic) phase may be chosen to be at $z=-\infty$ $(+\infty)$, and $-\infty\leq z\leq\infty$.

B. Results

It is worthwhile first mentioning results for the free energy $\sigma_{I\text{-}N_\parallel}$ of the interface between coexisting isotropic and planar nematic phases. These are shown in Fig. 5 as a function of the reduced elastic constant L, corresponding to both positive $(0\leq L<1)$ and negative $(L>1)$ ranges of the original elastic constant L_2. In the figure $\sigma_{I\text{-}N_\parallel}$ is normalized by the free energy $\sigma_{I\text{-}N_\perp}$ of the isotropic—homeotropic-nematic interface, calculated in parabolic approximation. The latter has the value [in our reduced units, cf. (2.12)] $\sigma_{I\text{-}N_\perp}=\sqrt{2}/4$, in contrast to the exact model result $\sqrt{2}/6$. The limiting value of the ratio $\sigma_{I\text{-}N_\parallel}/\sigma_{I\text{-}N_\perp}$ as $L\to 0$ is $(3-\sqrt{3})/4\approx 0.317$. This number is bracketed in the figure by two points calculated using the exact result in the Sluckin-Poniewierski limit, $\sigma_{I\text{-}N_\parallel}(L=0)=0.105\,75\ldots$, normalized by either the exact or parabolic value of $\sigma_{I\text{-}N_\perp}$. A similar bracketing is shown using the numerically determined value[6] $\sigma_{I\text{-}N_\parallel}$

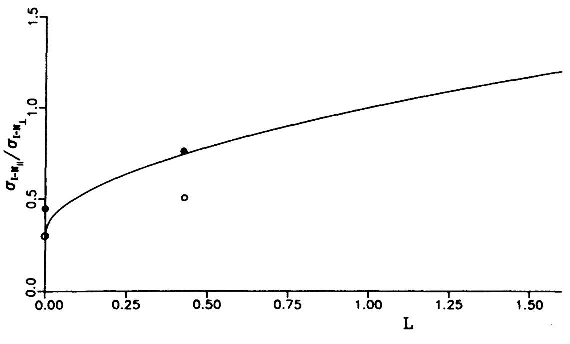

FIG. 5. Ratio of nematic-isotropic interfacial free energies vs reduced elastic constant L, in parabolic approximation. Circles give values of the ratio using exact results for $\sigma_{I\text{-}N_\parallel}$ at $L=\frac{3}{7}$ (Ref. 6) and $L=0$, corresponding to either exact (●) or approximate (○) values of $\sigma_{I\text{-}N_\perp}$.

$\simeq 0.178$ at $L=\frac{3}{7}$. While there are clearly quantitative discrepancies in the parabolic approximation, of more significance here is that the results show that the approximation is consistent with the predicted[16] orientational behavior at a free interface, favoring planar (homeotropic) alignment for positive (negative) values of L_2. The results to be described from now on will pertain to the experimentally expected range $L_2>0$.

We now focus on the limits of complete wetting by planar nematic layers of the wall—isotropic-phase interface, as a function of the interaction parameters c_m and elastic constant L. This regime turns out to be quite restricted. One can see this rather easily in the case $L=1$ (i.e., $L_2=0$), the opposite extreme to the Sluckin-Poniewierski limit $L=0$. At coexistence, and under the further simplification that $c_{2\eta}=c_{2\mu}\equiv c_2$—essentially the surface analog of the isotropic[31] elastic constant limit—we find explicitly[41]

$$\sigma_{W\text{-}I}(l)=\frac{\sqrt{2}}{4}+(c_2-c_1/2)-\frac{\sqrt{2}}{16}\frac{(c_1-4c_2)^2}{(\sqrt{2}c_2+1)}$$
$$+\frac{(c_1-4c_2)}{2(\sqrt{2}c_2+1)}e^{-\sqrt{2}l}+\frac{\sqrt{2}}{4}\frac{(\sqrt{2}c_2-1)}{(\sqrt{2}c_2+1)}e^{-2\sqrt{2}l}$$
$$-\frac{3\sqrt{2}}{16}\frac{c_1^2(2+e^{-6\sqrt{2}l})}{[2(\sqrt{2}c_2+3)+(\sqrt{2}c_2-3)e^{-6\sqrt{2}l}]}\;. \tag{4.8}$$

This expression becomes singular as $c_2\rightarrow(-1/\sqrt{2})$ from above; see also our remark before (4.7). Similar singularities are encountered in more general cases when $c_{2\mu}$ and/or $c_{2\eta}$ become sufficiently negative; those associated with negative $c_{2\eta}$ are believed to signal the collapse of the parabolic approximation in situations of strong surface enhancement, cf. Fig. 3, while those associated with negative $c_{2\mu}$ are related to the twist instability described at the end of Sec. III. Away from such regions, we can apply well-known arguments[1,14,26,38] to discern the stable wetting states of $\sigma_{W\text{-}I}(l)$. In particular, complete wetting by $N_\parallel$ occurs when the global minimum of $\sigma_{W\text{-}I}(l)$ lies at $l=\infty$. Analysis of (4.8) reveals, however, that $\sigma_{W\text{-}I}(l=\infty)$ is smaller than $\sigma_{W\text{-}I}(l=0)$ only when $c_2<0$, and then only for values of c_1 in a finite interval $c_1^{(-)}\leqq c_1\leqq c_1^{(+)}$, where $c_1^{(\pm)}$ are given as a special case of (4.9) below. Within this interval $\sigma_{W\text{-}I}(l=\infty)$ yields the global minimum of the free energy and hence complete wetting is stable. Otherwise, the global minimum occurs at $l=0$, which corresponds to partial wetting by planar, but *uniaxial,* nematic layers. What is striking is the existence of an upper limit $c_1^{(+)}$ to the surface field c_1 beyond which complete wetting is not stable. This is reminiscent of the reentrant wetting behavior exhibited by solid films.[20,21]

Essentially the same picture is obtained when we allow $c_{2\eta}$ and $c_{2\mu}$ to differ. Still keeping $L=1$, a somewhat more involved analysis again shows that complete wetting by $N_\parallel$ occurs only in the domain $c_{2\mu}<0$, $c_1^{(-)}\leqq c_1\leqq c_1^{(+)}$, where

$$c_1^{(\pm)}=\frac{\sqrt{2}}{3}\{(\sqrt{2}c_{2\eta}+1)(\sqrt{2}c_{2\mu}+3)$$
$$\pm 2[\sqrt{2}|c_{2\mu}|(\sqrt{2}c_{2\eta}+1)D]^{1/2}\}(\sqrt{2}c_{2\mu}+1)^{-1}\,, \tag{4.9}$$
$$D=6+5\sqrt{2}c_{2\mu}+3\sqrt{2}c_{2\eta}+4c_{2\eta}c_{2\mu}\;.$$

This result holds for arbitrarily large *positive* values of $c_{2\eta}$; the common value of $c_1^{(\pm)}$ as $c_{2\mu}\rightarrow 0^-$ is described by the line $c_1^{(\pm)}=2c_{2\eta}+\sqrt{2}$. Instabilities now transpire as either $c_{2\mu}$ or $c_{2\eta}$ approaches the value $-1/\sqrt{2}$. One notes that $c_1^{(-)}<0$ for sufficiently negative values of $c_{2\mu}$. In such a range of c_1, we can expect to find (cf. Fig. 3) competition between planar and homeotropic nematic wetting layers. The significance of such competition is subject to the same doubts expressed in in Sec. III, so we have not examined it in detail.

When $L<1$, the algebraic complexity of the model solutions precludes obtaining concise analytic expressions for the free energy, and we have relied on numerical scans of $\sigma_{W\text{-}I}(l)$. We find that the features described above are shifted in the direction of positive $c_{2\mu}$. This is indicated by the phase diagram in Fig. 6, corresponding to the (empirically large) ratio value $L_2/L_1=10$, which exhibits the dome-shaped surface of wetting and, at larger values of c_1, *dewetting* transitions in the three-dimensional $(c_1,c_{2\mu},c_{2\eta})$ space. Consistent with the discussion given above, the transitions across most of that surface are first order. In addition, however, there now appears a section of continuous wetting transitions at large, positive $c_{2\eta}$, and negative $c_{2\mu}$. As required by the argument near the end of Sec. IV A, each continuous wetting transition is preceded by a first-order uniaxial to biaxial symmetry-breaking transition (similar to what is called, in a related context, a "partial wetting" transition[42]). The surface representing the latter transitions is not exhibited in Fig. 6, but is actually the smooth continuation of the surface of first-order wetting transitions. All three surfaces meet along the dashed seam in the figure, which is a line of critical endpoints. Notice that a slice through the diagram at constant $c_{2\mu}$ which intersects that seam would generate a phase diagram similar to that in the upper right corner of Fig. 3, if we overlook both the first-order

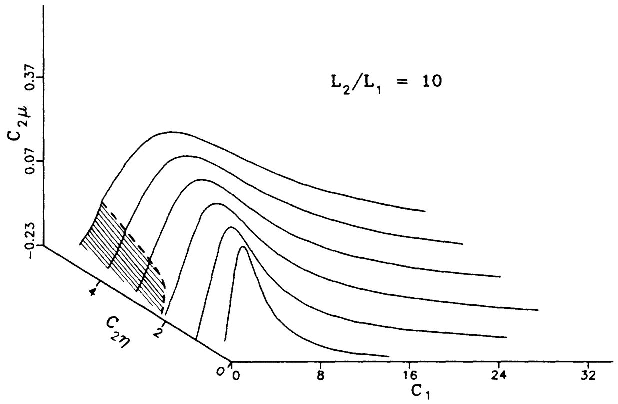

FIG. 6. Domain of complete wetting by planar nematic in parabolic approximation, for $L_2/L_1=10$. Solid lines show loci of wetting and dewetting transitions, $c_{2\mu}$ vs c_1 at different fixed values of $c_{2\eta}$, such that complete wetting occurs in region underneath those curves. The ruled section indicates domain of continuous wetting transitions.

nature of the present symmetry-breaking transitions and the dewetting transitions at larger values of c_1.

One could question whether the occurrence of dewetting is simply an artifact of the constrained trajectories we have so far considered, and whether a reentrant trajectory such as indicated in Fig. 4(a) might allow for stable wetting states when $c_1 > c_1^{(+)}$. We have examined this point using the fact that the wall-isotropic free energy of a complete-wetting configuration necessarily obeys Antonow's rule,

$$\sigma_{W\text{-}I} = \sigma_{W\text{-}N_{\parallel}} + \sigma_{I\text{-}N_{\parallel}} \; . \tag{4.10}$$

The reentrant trajectory of Fig. 4(a) for $\sigma_{W\text{-}I}$ may be decomposed into individual segments associated with $\sigma_{W\text{-}N_{\parallel}}$ and $\sigma_{I\text{-}N_{\parallel}}$, each of which has only a single crossing between nematic and isotropic domains and hence can be computed by methods already described. The resulting $\sigma_{W\text{-}I}$ would support complete nematic wetting if its value is smaller than $\sigma_{W\text{-}I}(l=0)$ of (4.7). (This procedure cannot reveal whether a reentrant *partial* wetting trajectory could be of yet lower free energy, but we believe that to be unlikely.) Asymptotic analysis of $\sigma_{W\text{-}N_{\parallel}}$ in the limit of large c_1, whose details we shall omit, shows that reentrant trajectories do allow for stable wetting states and prevent dewetting when L_2/L_1 is greater than 15.77.... In this regime the phase diagram of Fig. 6 is replaced by one exhibiting a single-valued surface of wetting transitions, such that complete wetting by $N_{\parallel}$ always occurs if c_1 is made sufficiently large. An important consequence is that, in this range of L_2/L_1, the solutions of the parabolic approximation *qualitatively* reproduce most of the features of the Sluckin-Poniewierski[13] model at coexistence. For example, when $c_{2\mu}$ is greater than a small positive value depending on L_2/L_1, all complete-wetting states are associated with reentrant trajectories. As c_1 increases, the corresponding initial value $\mu(0)$ approaches very close to zero. This is similar to the behavior found in the Sluckin-Poniewierski model for nonzero values of $c_{2\mu}$, described at the end of Sec. III.

We draw attention in Fig. 4(b) to the typical behavior of phase-space trajectories in the vicinity of a continuous wetting transition, showing a pair of trajectories appropriate to states close to but on opposite sides of the transition. One observes that, in contrast to the behavior of all one-component Landau models and of that assumed in the multicomponent models of Refs. 38 and 39, the continuous transition does not proceed with the initial point $(\eta(0),\mu(0))$ passing through the bulk fixed point. Instead, a section of the trajectory *away* from the initial point approaches the fixed point. Those sections of the complete-wetting trajectories in Fig. 4 which encompass that of the free nematic-isotropic interface should be compared with the trajectory in the Sluckin-Poniewierski model, cf. Fig. 2.

We have performed a few studies relevant to the regions of isotropic wetting and nearby homeotropic-planar orientational transitions, cf. Fig. 3. The behavior at coexistence in these regions differs little from that sketched in Sec. III, as was anticipated from arguments given there. The major effect of the parameter $c_{2\mu}$ is to vary the relative extent of continuous and first-order wetting transitions, in favor of the former when $c_{2\mu}$ grows positive while inhibiting them when $c_{2\mu}$ becomes negative. A significant departure from the behavior described earlier emerges away from coexistence, i.e., at $t<1$. It is a basic feature of the Sluckin-Poniewierski model [cf. Fig. 2 and (3.1)] that the trajectory $\mu^*(\eta)$ of that model always traverses the isotropic fixed point and is strictly uniaxial at positive values of η, for all $0<t<1$. This remains true of all complete isotropic-wetting trajectories at coexistence in the parabolic approximation. For $t<1$ and $L>0$, however, the trajectories to the bulk $N_{\parallel}$ fixed point which evolve continuously from those at coexistence do not, indeed cannot in parabolic approximation, maintain μ strictly zero at any value of η. This gives rise to unphysical solutions characterized by positive η but nonzero μ near the wall, i.e., weakly biaxial states in homeotropic alignment. While we do not rule out that a better approximation could change this, we believe it is more likely that director distortion occurs. That indeed would be consistent with the tilt-angle measurements[36] mentioned in Sec. III.

V. DISCUSSION

It is conceivable that our finding of limited ranges of complete wetting by planar nematic films is due to inadequacy of the parabolic approximation. After all, the reentrant trajectories which are necessary for wetting at high substrate energy c_1 sample regions of the (η,μ) phase plane far from either of the fixed points about which the function $f_L(\eta,\mu)$ has been expanded. Nonetheless, a qualitative argument indicates that the result derived below (4.10), i.e., the existence of a lower limit to the ratio L_2/L_1 below which reentrant trajectories are unable to stabilize complete wetting, may be of general validity. We suggest that the free energy $\sigma_{W\text{-}I}$ associated with a reentrant trajectory whose initial value $\mu(0)$ is close to zero, *relative* to that of a uniaxial trajectory with $\mu=0$ for all z, is largely controlled by two opposing factors. These are the tendencies to minimize $f_L(\eta,\mu)$ at fixed η, which yields the Sluckin-Poniewierski trajectory $\mu^*(\eta)$ in Fig. 2, and to minimize the elastic term $(L\dot{\mu}^2/2)$, cf. (2.17), which clearly favors the nonwetting uniaxial trajectory. It is plausible that for sufficiently large L, i.e., small L_2/L_1, the elastic term always dominates and prevents wetting.

Let us conclude with comments on a few remaining issues. The present mean-field approach neglects fluctuation effects, which tend to inhibit long-range order in continuous-symmetry systems of reduced dimensionality. It was suggested in Ref. 13 that fluctuations would convert all continuous uniaxial-biaxial transitions into defect-unbinding transitions of the Kosterlitz-Thouless type. By analogy to the absence of first-order surface transitions in *two-dimensional* Ising models[43] and in three-dimensional *isotropic* n-component models,[44] fluctuations may have the further effect of changing some or all of the present first-order wetting transitions into continuous ones. In view of some recent results for systems with planar-spin symmetry,[45,46] however, first-order transitions do not appear to be entirely excluded. Differences between the symmetries characterizing nematic liquids and continuous-spin models[47] lead to additional uncertainties.

It is universally observed that the director at a free nematic-isotropic interface is obliquely tilted, which as often remarked is contrary to the predictions of Landau—de Gennes theory. That "universality" is strongly suggestive of a fluctuation-induced mechanism. On the other hand, anisotropies present in all real nematic liquids but neglected in the basic Landau—de Gennes model, e.g., biaxial molecular shape, could be playing a major role. Higher-level order parameters, in particular averages of fourth-rank spherical harmonics, could also be significant. Inclusion of these in mean-field models accounts for a major part of the observed difference between the Frank elastic constants K_{11} and K_{33},[31,32] and, of particular relevance, provides a mechanism for obtaining so-called "tilted uniaxial" smectic-A liquid crystals.[48]

It is possible to generalize the parabolic approximation of Sec. IV to treat cases of director distortion, i.e., spatially varying tilt angle $\psi(z)$. One important difference which arises (in terms of the original principal-axis order parameters described in Sec. II) is that the local free-energy density f_L is independent of ψ. Hence there is no *a priori* "fixed-point" value of ψ associated with the nematic region. Such a value can be introduced in a generalized parabolic approximation but must be treated as a variational parameter. Applications of this method will be described in future work.

An important feature which is expected to result from director distortion is the occurrence of an asymptotic power-law term proportional to l^{-1} in the free energy as a function of the wetting-layer thickness l.[34] This is similar to the strain-induced effect characterizing solid films,[21] but unlike the latter, appears to stabilize rather than destabilize the growth of wetting layers.[34] The full consequences of this effect remain to be investigated.

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APPENDIX: ON SURFACE TERMS IN LANDAU—de GENNES THEORY

Here we outline how the Landau—de Gennes free-energy functional (2.3) can be derived from a mean-field model[4,27] which explicitly exhibits the role of molecular interactions, focusing on the genesis of the surface term f_S. This treatment closely parallels ones which have been used to derived Landau-type functionals for surfaces in Ising models[25] and simple fluids.[49] As in the text, we suppose that the nematic fluid occupies the semi-infinite volume $z \geq 0$, bounded by a flat wall at $z=0$, although more general situations could be considered. The free energy F is a functional of the single-particle probability density $\rho(z\omega)$, where ω denotes the Euler angles characterizing the orientation of a molecule and where spatial variation in the single direction z has been assumed. The prototypical form of F is[4,27]

$$F=\int_0^\infty dz\, f_0([\rho(z\omega)])+\int_0^\infty dz\, d\omega\, \rho(z\omega)U(z\omega) + \tfrac{1}{2}\int_0^\infty dz_1 d\omega_1 \int_0^\infty dz_2 d\omega_2 \rho(z_1\omega_1) \times V(\,|z_{12}|\,\omega_1\omega_2)\rho(z_2,\omega_2)\;, \tag{A1}$$

where $U(z\omega)$ is the potential on a molecule due to the wall and $V(\,|z_{12}|\,\omega_1\omega_2)\equiv V(12)$ is the intermolecular pair potential (usually excluding contributions from short-distance repulsive interactions) integrated over relative spatial coordinates parallel to the surface. The symmetry implied by uniaxial molecules with an inversion center has been invoked to express $V(12)$ as an even function of $z_{12}\equiv z_2-z_1$. The quantity f_0 in (A1) represents other *spatially local* contributions to the free energy, but is generally a *functional* of the orientational distribution,[4,27] as indicated by the square brackets [ ] in (A1).

We proceed to reduce the nonlocal, two-body term in (A1), by making a formal gradient expansion of $\rho(z\omega)$, although this is not always well justified for values of z near zero.[25] An intermediate step in this procedure is a rearrangement of that term, denoted F_2, following the method of Teletzke, Scriven, and Davis.[49] To quadratic order in the gradient $\dot{\rho}(z\omega)\equiv d\rho(z\omega)/dz$, we obtain

$$F_2 \simeq \tfrac{1}{2}\int_0^\infty dz\, d\omega_1 d\omega_2 V_0(z\omega_1\omega_2)\rho(z\omega_1)\rho(z\omega_2) - \tfrac{1}{4}\int_0^\infty dz\, d\omega_1 d\omega_2 V_2(z\omega_1\omega_2)\dot{\rho}(z\omega_1)\dot{\rho}(z\omega_2)\;, \tag{A2}$$

where

$$V_m(z\omega_1 w_2)=\int_{-z}^{\infty} dx\, x^m V(\,|x|\,\omega_1\omega_2)\;. \tag{A3}$$

The dependence of the functions V_m on z is a consequence of the semi-infinite ranges of integration in the initial expression (A1) (Ref. 49) and would not arise if those integrations were over all space. If, as we shall henceforth suppose, the pair potential $V(12)$ vanishes for separations $|z_{12}|$ greater than some microscopic distance R, then $V_m(z\omega_1\omega_2)$ reduces to a function $V_m(\omega_1\omega_2)$ independent of z when $z>R$. In this case, if it is also supposed that the external potential $U(z\omega)$ vanishes or becomes independent of z when $z>R$, the free-energy density implied by (A1) and (A2) acquires for $z>R$ the same form as obtained in an infinite domain in the absence of the wall. This would likewise be true of the Euler-Lagrange equations for $\rho(z\omega)$ generated by variation of F. Now it is a consequence of the (spatially) *second-order* nature of those equations that the free energy F could always be written as a semi-infinite integral of that free-energy density obtained in the absence of the wall, plus an additional term to account for the latter

$$\begin{aligned}F=&\int_0^\infty dz\, f_0([\rho_e(z\omega)])\\&+\tfrac{1}{2}\int_0^\infty dz\, d\omega_1 d\omega_2 V_0(\omega_1\omega_2)\rho_e(z\omega_1)\rho_e(z\omega_2)\\&-\tfrac{1}{4}\int_0^\infty dz\, d\omega_1 d\omega_2 V_2(\omega_1\omega_2)\dot{\rho}_e(z\omega_1)\dot{\rho}_e(z\omega_2)\\&+f_s([\rho_e(0\omega)])\ .\end{aligned}\tag{A4}$$

Here $\rho_e(z\omega)$ equals the actual distribution function $\rho(z\omega)$ in the outer region $z\geq R$ and is the smooth "extrapolation"[15] of that function in the layer $0\leqq z<R$. The relation (A4) can be viewed as *defining* the surface term $f_S([\rho_e(0\omega)])$ as a functional of the extrapolated probability density at $z=0$. In general, f_S could be determined only by solving for the true probability density $\rho(z\omega)$ in the layer. Despite the formal nature of this result, it is important to recognize that f_S does not depend on spatial gradients of $\rho_e(0\omega)$. Applying an analogous argument to derivations of the Frank elastic energy[50] shows that terms involving surface normal gradients of the extrapolated[15] nematic director, associated with the Nehring-Saupe[51] elastic constant K_{13}, should never contribute.[29]

An approximate estimate of f_S agreeing with results derived for a nearest-neighbor Ising model[25] can be obtained by neglecting both the difference $\rho_e(z\omega)-\rho(z\omega)$ as well as gradients of the distribution function in the layer $0<z<R$. The f_S found by comparing (A4) with (A1) and (A2) under this recipe receives contributions simply from the external potential $U(0\omega)$ and from "broken" pair bonds. We apply this to a model potential which is consistent with the type of molecular symmetry and level of orientational order parameters retained in classical Landau—de Gennes and Maier-Saupe[52] theory. In a Cartesian tensor representation, this reads[23,53]

$$\begin{aligned}V(z\omega_1\omega_2)=&g_1(z)\hat{\mathbf{k}}\cdot(\underline{q}_1+\underline{q}_2)\cdot\hat{\mathbf{k}}+g_2(z)\mathrm{Tr}(\underline{q}_1\cdot\underline{q}_2)\\&+g_3(z)(\hat{\mathbf{k}}\cdot\underline{q}_1\cdot\hat{\mathbf{k}})(\hat{\mathbf{k}}\cdot\underline{q}_2\cdot\hat{\mathbf{k}})\\&+g_4(z)\hat{\mathbf{k}}\cdot(\underline{q}_1\cdot\underline{q}_2)\cdot\hat{\mathbf{k}}\ ,\end{aligned}\tag{A5}$$

where [cf. (2.1)]

$$\underline{q}_i=\underline{q}(\omega_i)=\tfrac{1}{2}[3\hat{\mathbf{e}}(\omega_i)\hat{\mathbf{e}}(\omega_i)-\underline{I}]\ .\tag{A6}$$

Similarly, the potential due to the wall will be represented by

$$U(z\omega)=U(z)\hat{\mathbf{k}}\cdot\underline{q}(\omega)\cdot\hat{\mathbf{k}}\ .\tag{A7}$$

We have neglected any contributions to V and U which are independent of the microscopic ordering tensor $\underline{q}(\omega)$. Likewise, in evaluating the free energy, we shall ignore any spatial variation of the angle-averaged number density $\rho_n\equiv\int d\omega\,\rho(z\omega)$. (Effects of these have been considered in Refs. 4 and 27.) Recalling (2.1), we find that the surface-excess part of (A4) agrees with the free-energy functional defined in (2.3)—(2.6), given the following relations:

$$f_L(\underline{Q})=f_0(\underline{Q})-a_2\mathrm{Tr}\underline{Q}^2\ ,\tag{A8a}$$

$$a_2=-\rho_n^2\int_0^R dz\, g_2(z)\ ,\tag{A8b}$$

$$L_m=-\rho_n^2\int_0^R dz\, z^2 g_{2m}(z),\quad m=1,2\tag{A8c}$$

$$c_1=\rho_n\int_0^R dz\, u(z)-\rho_n^2\int_0^R dz\, z g_1(z)\ ,\tag{A8d}$$

$$c_m=-\frac{\rho_n^2}{2}\int_0^R dz\, z g_m(z),\quad m=2,3,4\ .\tag{A8e}$$

The quantity a_2 can be identified with the Maier-Saupe interaction parameter.[52] [Given a suitable model for $f_0(\underline{Q})$, a further Landau expansion of (A8a) would give agreement with (2.4).] We remark that constants a_m defined analogous to (A8b) in terms of the functions $g_1(z)$, $g_3(z)$, and $g_4(z)$ are zero, and similarly that $g_3(z)$ does not contribute a gradient coefficient analogous to L_1 and L_2. These properties reflect the correct rotational invariances of the integrals $V_0(\omega_1\omega_2)$ and $V_2(\omega_1\omega_2)$.[23,33] In contrast, there is no necessity for any of the integrals in (A8d) and (A8e) to vanish.

Let us further remark that stability conditions requiring a_2 and L_1 to be positive[16,30] suggest, on the model above, that the surface coefficient c_2 should be positive as well. This need not be true in general of the coefficient c_4, but is in the expected case (see Sec. II B) that $L_2>0$. The coefficients c_3 could be of arbitrary sign; model calculations[33] indicate that its magnitude is usually small compared with that of c_2 and c_4. Then one expects that the coefficient $c_{2\eta}$ defined in (2.20) is normally positive. These assignments, however, only hold insofar as the approximate derivation of f_S given here is valid. Furthermore, as in other contexts,[14,25] a generalization of the model to include surface enhancement of the pair potential between molecules in the layer $0<z<R$ could lead to opposite signs of the coefficients.

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