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Phenomenological theory of smectic-A liquid crystals

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A generalization of the Landau–de Gennes phenomenological theory of smectic-A liquid crystals is described. The theory is based on a Landau-Ginzburg free energy that includes local and nonlocal parts. The local part consists of the isotropic-Ising-model free energy and de Gennes's phenomenological free energy of the nematic phase. The nonlocal part is derived from the form of two-body contributions to the free energy in molecular density-functional theories, expanded in gradients of the number density and orientational order parameter. A mean-field approximation to the theory is analyzed by both Landau expansion and by a full numerical solution, involving Fourier-series representations of the number density and an orientational order parameter with an appropriately large number of Fourier coefficients. The main purpose of the analysis is to show that the smectic phase results from the instability of a uniform phase induced by the gradient terms in the free energy, particularly those that couple modulations in the density and orientational order parameter.

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I. INTRODUCTION

Although smectic liquid crystals have been extensively studied [1], there is not yet a fully satisfactory understanding of these phases. Previous theoretical studies are mainly of two types: molecular mean-field theories, following the works of MacMillan [2] and Kobayashi [3], and phenomenological Landau–de Gennes (LdG) theories [1,4]. A critique of the previous mean-field theories, and a reformulation of these theories, has recently been given by Mederos and Sullivan [5].

The LdG theory is based on the following ideas. The nematic phase breaks the continuous rotational symmetry of the isotropic liquid phase in that the molecules have an average orientation given by the director $\hat{\mathbf{n}}$. The degree of orientational order in the direction $\hat{\mathbf{n}}$ is usually indicated by the order parameter $\overline{\eta}=\langle P_2(\cos\theta)\rangle$, where θ is the angle between the molecular axis and the director $\hat{\mathbf{n}}$ and $\langle\ \rangle$ denotes a statistical average. The structure of the smectic-A phase consists of layers parallel to $\hat{\mathbf{n}}$ with thickness d of the order of the molecular length, so that the continuous translational symmetry in the direction parallel to $\hat{\mathbf{n}}$ is broken. Assuming that the layer normal is on average parallel to the z direction, there is a density modulation $\rho(\mathbf{r})=\rho_0\{1+\mathrm{Re}[\psi(\mathbf{r})e^{iqz}]\}$, where $\psi(\mathbf{r})$ is the complex smectic order parameter. Here $q=2\pi/d$, and $\psi(\mathbf{r})$ is assumed to vary spatially on a length scale larger than d. The LdG Helmholtz free-energy density, which includes fluctuations of the director $\hat{\mathbf{n}}$ and of ψ, is

$$
\begin{aligned}
f(\psi,\delta\hat{\mathbf{n}})=&\tfrac{1}{2}A|\psi|^2+\tfrac{1}{4}C|\psi|^4+\frac{1}{2M_\parallel}|\nabla_\parallel\psi|^2\\
&+\frac{1}{2M_\perp}|\nabla_\perp-iq\delta\hat{\mathbf{n}})\psi|^2\\
&+\tfrac{1}{2}[K_1(\nabla\cdot\delta\hat{\mathbf{n}})^2+K_2(\hat{\mathbf{n}}\cdot\nabla\times\delta\hat{\mathbf{n}})^2\\
&+K_3(\hat{\mathbf{n}}\times\nabla\times\delta\hat{\mathbf{n}})^2]\ , \qquad (1.1)
\end{aligned}
$$

where $\delta\hat{\mathbf{n}}$ is the director fluctuation about the z direction. This free energy includes a mean-field contribution in even powers of the amplitude $|\psi|$. Odd powers of ψ do not appear because a change in sign, $\psi\rightarrow-\psi$, corresponds to a uniform translation of the smectic layers by $d/2$. The other contributions in (1.1) depend on gradients of $\hat{\mathbf{n}}$ and ψ, accounting for the free energy associated with long-wavelength distortions in these variables and consistent with rotational symmetry. Many studies of this model have been carried out [6,7] aimed at determining the critical behavior at a continuous nematic-smectic transition, although there is not yet a full consensus on the theoretical predictions of the model.

There are several limitations associated with the LdG model: (1) As remarked elsewhere [8], the coefficients that appear in (1.1) are phenomenological and their relation to molecular properties is not revealed. (2) Only the first Fourier coefficient in the density has been retained. This limits the application of the theory to the region near a second-order nematic-smectic phase transition. (3) The layer spacing $d=2\pi/q$ is assumed to be constant (on the order of a molecular length). A more complete theory should treat d as a variational parameter. (4) Finally, and perhaps most importantly, the free energy (1.1) is considered to involve independent fluctuations only in the quantities ψ and $\hat{\mathbf{n}}$. Fluctuations in the orientational order parameter $\overline{\eta}=\langle P_2(\cos\theta)\rangle$ are assumed to be related to those in the density in exactly the same way as in the nonfluctuating state, and have been eliminated by free-energy minimization [1,4]. Since, as we shall see, a crucial role in driving the underlying "mean-field" transition is due to the coupling between $\overline{\eta}$ and ρ, one might question the validity of this procedure.

In this paper we shall present a theory which overcomes some of the difficulties noted above. In particular, we shall derive a "Landau-Ginzburg" free energy for a liquid crystal which contains coupled gradients in all the relevant variables ρ, $\overline{\eta}$, and $\hat{\mathbf{n}}$. This free energy is derived by reference to previous molecular density-functional theories, although we believe its form to be of more general validity. In this paper, we limit the analysis of the free energy to a mean-field treatment. The main purposes are to demonstrate (1) how the gradient terms in the free energy lead to instability of a uniform phase with respect to formation of a smectic phase and (2) that this instability depends crucially on coupling between density and orientational order parameters [9].

The theory is presented in Sec. II A. Section II B discusses calculational details, in particular, on obtaining numerically exact solutions of the theory in contrast with the more common analyses using low-order Fourier series. The application of a Landau expansion of the smectic free energy is described in Sec. II C. Numerical results are given in Sec. III, while Sec. IV contains a closing discussion.

II. THEORY

A. Free-energy functional

The form of the theory that we are seeking is motivated by the well-known Landau-Ginzburg free energy (or "Hamiltonian") for a system characterized by a single order parameter $\phi(\mathbf{r})$,

$$F_{\mathrm{LG}}=\int dr[\tfrac{1}{2}(\nabla\phi)^2+f_L(\phi)] ,$$

where $f_L(\phi)$ is usually given by the local free-energy density of the uniform phase. In the case of a smectic phase, the free energy should be functional of two fundamental order parameters, the number density $\rho(\mathbf{r})$, and the orientational order parameter tensor,

$$\mathsf{Q}=\int d\omega\, f(\omega)\mathsf{q}=\tfrac{1}{2}\int d\omega\, f(\omega)[3\hat{\mathbf{e}}(\omega)\hat{\mathbf{e}}(\omega)-\mathsf{I}] , \tag{2.1}$$

where $\hat{\mathbf{e}}(\omega)$ is a unit vector along the symmetry axis of the molecule, I is the unit tensor, and $f(\omega)$ is the normalized distribution function of the molecular orientation, the latter denoted by ω. A bulk nematic phase usually has uniaxial symmetry with respect to the director $\hat{\mathbf{n}}$, in which case Q becomes

$$\mathsf{Q}=\frac{\overline{\eta}}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}}-\mathsf{I}) , \tag{2.2a}$$

where

$$\overline{\eta}=\langle P_2(\cos\theta)\rangle=\int d\omega\, f(\theta)P_2(\cos\theta) , \tag{2.2b}$$

where θ is the angle between the molecular axis and $\hat{\mathbf{n}}$, and P_2 is the second Legendre polynomial. We shall assume throughout this paper that Q has the uniaxial form (2.2), although strictly speaking this is true only if the system is nonuniform in a single direction coinciding with $\hat{\mathbf{n}}$.

What distinguishes the smectic phase from nematic and isotropic phases is the existence of nonvanishing gradients of $\rho(\mathbf{r})$ and $Q(\mathbf{r})$. Therefore we identify the local free-energy density f_L with that describing bulk nematic and isotropic fluids, and which exhibits local (or possibly global) minima appropriate to these phases. The nonlocal gradient terms in the free energy should then be such that under appropriate conditions, those terms led to an instability of the uniform (isotropic or nematic) phase with respect to formation of a modulated phase.

We shall proceed by dividing the Helmholtz free energy F into local and nonlocal parts

$$F=F_L+F_{\mathrm{NL}} . \tag{2.3}$$

The local free energy F_L is in turn given by

$$F_L=F_{0,L}+F_{A,L} . \tag{2.4}$$

Here $F_{0,L}$ and $F_{A,L}$ are isotropic and anisotropic local free energies, respectively. This separation of the local free energy into isotropic and anisotropic contributions is consistent with approximate molecular density-functional theories [10]. For simplicity, $F_{0,L}$ is modeled by the standard quartic-order Landau-Ginzburg free energy describing liquid-vapor phase separation in an isotropic fluid,

$$F_{0,L}=\int dr\, f_{0,L}=\int dr\left[\frac{a}{2}(T-T_c)(\rho-\rho_c)^2+\frac{b}{4}(\rho-\rho_c)^4\right] , \tag{2.5}$$

where T and ρ are the temperature and density, respectively, T_c and ρ_c are the liquid-vapor critical temperature and density, and a and b are constants. The anisotropic local free energy is modeled after de Genne's free energy [1] for nematic liquid crystals

$$F_{A,L}=\int dr\, f_{A,L}=\int dr\, \rho(A_Q\overline{\eta}^2-B_Q\overline{\eta}^3+C_Q\overline{\eta}^4) , \tag{2.6a}$$

where $\overline{\eta}$ is the nematic order parameter. Following de Gennes, the temperature dependence of B_Q and C_Q is neglected, while usually A_Q is taken to vary linearly with temperature. A slightly more general model is one in which A_Q varies linearly with both temperature and density [10]

$$A_Q=A_0+A_1T-A_2\rho . \tag{2.6b}$$

We now consider the nonlocal part of the free energy in Eq. (2.3). We base our analysis of this part on the typical form of two-body contributions to the free energy occurring in mean-field density-functional theories [5,8,10]:

$$F_{\mathrm{NL}}=\tfrac{1}{2}\int d\mathbf{r}_1 d\omega_1\int d\mathbf{r}_2 d\omega_2\, \rho(\mathbf{r}_1\omega_1)V(\mathbf{r}_{12},\omega_1,\omega_2)\rho(\mathbf{r}_2\omega_2) , \tag{2.7}$$

where the one-particle probability density $\rho(\mathbf{r}_i\omega_i)$ varies with position $\mathbf{r}_i$ and molecular orientation ω_i. The interaction potential $V(\mathbf{r}_{12},\omega_1,\omega_2)$ depends on the separation vector $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ and the orientations ω_1 and ω_2 of the molecules.

Defining new coordinates $\mathbf{r}$ and $\mathbf{R}$ by

$$\mathbf{r}=\mathbf{r}_{12} ,$$

$$\mathbf{R}=\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2) ,$$

and doing a Taylor-series expansion in powers of $\mathbf{r}$ we get, to quartic order,

$$F_{\mathrm{NL}}=\tfrac{1}{2}\int d\omega_1 d\omega_2 \int d\mathbf{R}\, d\mathbf{r}\, V(\mathbf{r},\omega_1,\omega_2)[\rho(\mathbf{R}\omega_1)\rho(\mathbf{R}\omega_2)-\tfrac{1}{2}\tilde{\nabla}\rho(\mathbf{R}\omega_1)\tilde{\nabla}\rho(\mathbf{R}\omega_2)+\tfrac{1}{24}\tilde{\nabla}^2\rho(\mathbf{R}\omega_1)\tilde{\nabla}^2\rho(\mathbf{R}\omega_2)] \;, \tag{2.8}$$

where $\tilde{\nabla}\equiv\mathbf{r}\cdot\nabla_{\mathbf{R}}$. In the above expansion, several integrations by parts in $\mathbf{R}$ (neglecting surface contributions) have been performed, and the symmetry $V(\mathbf{r},\omega_1,\omega_2)=V(\mathbf{r},\omega_2,\omega_1)$ has been assumed.

We write

$$V(\mathbf{r},\omega_1,\omega_2)=V_0(r)+V_A(\mathbf{r},\omega_1,\omega_2) \;, \tag{2.9}$$

where $V_0(r)$ is an isotropic interaction energy which depends only on the separation distance $r=|\mathbf{r}|$, and $V_A(\mathbf{r},\omega_1,\omega_2)$ is an anisotropic interaction which depends on the molecular orientations ω_i as well as the separation vector $\mathbf{r}$. Consider first the contribution of the isotropic potential; upon substituting $V_0(r)$ into (2.8), we obtain for the isotropic nonlocal free energy

$$F_{0,\mathrm{NL}}=\tfrac{1}{2}\int d\mathbf{R}\{A\rho^2(\mathbf{R})+B[\nabla\rho(\mathbf{R})]^2+C[\nabla^2\rho(\mathbf{R})]^2\} \;, \tag{2.10a}$$

where

$$A=\int d\mathbf{r}\, V_0(r) \;, \tag{2.10b}$$

$$B=-\tfrac{1}{6}\int d\mathbf{r}\, r^2 V_0(r) \;, \tag{2.10c}$$

$$C=\tfrac{1}{120}\int d\mathbf{r}\, r^4 V_0(r) \;, \tag{2.10d}$$

and $\rho(\mathbf{R})=\int d\omega\rho(\mathbf{R}\omega)$ is the angle-averaged density. The first term in $F_{0,\mathrm{NL}}$, involving $A\rho^2$, can be absorbed into $F_{0,L}$ [Eq. (2.5)] and the remainder gives the isotropic nonlocal free energy. For a bulk smectic phase it is appropriate to assume spatial variation along the z direction only, in which case the free energy per unit area is given by

$$\frac{F_{0,\mathrm{NL}}}{A}=\tfrac{1}{2}\int dz \left[B\left[\frac{d\rho}{dz}\right]^2 + C\left[\frac{d^2\rho}{dz^2}\right]^2 \right] \;, \tag{2.11}$$

where henceforth A denotes the cross-sectional area of the system.

Consider now the anisotropic part of the interaction in (2.9); following Ronis and co-workers [8] we model this as

$$\begin{aligned} V_A(\mathbf{r},\omega_1,\omega_2)={}&g_1(r)\hat{\mathbf{r}}\hat{\mathbf{r}}:(\mathbf{q}_1+\mathbf{q}_2)+g_2(r)\mathbf{q}_1:\mathbf{q}_2 \\ &+g_3(r)(\hat{\mathbf{r}}\hat{\mathbf{r}}:\mathbf{q}_1)(\hat{\mathbf{r}}\hat{\mathbf{r}}:\mathbf{q}_2)+g_4(r)\hat{\mathbf{r}}\cdot\mathbf{q}_1\cdot\mathbf{q}_2\cdot\hat{\mathbf{r}} \;, \end{aligned} \tag{2.12}$$

where $\hat{\mathbf{r}}=\mathbf{r}/r$, and

$$\mathbf{q}_i=\mathbf{q}(\omega_i)=\tfrac{1}{2}(3\hat{\mathbf{e}}_i\hat{\mathbf{e}}_i-\mathsf{I}) \;, \tag{2.13}$$

where $\hat{\mathbf{e}}_i$ is the unit vector along the symmetry axis of molecule i. The potential defined in Eq. (2.12) is the most general anisotropic potential one can construct that is linear in each $\mathbf{q}_i$, and is equivalent to an expansion up to second-order spherical harmonics of both ω_1 and ω_2 [11].

Substituting V_A into (2.8) and assuming spatial variation in the z direction only, we obtain for the anisotropic nonlocal free energy

$$F_{A,\mathrm{NL}}=F_{A,\mathrm{NL}}^{(2)}+F_{A,\mathrm{NL}}^{(4)} \;, \tag{2.14}$$

$$\frac{F_{A,\mathrm{NL}}^{(2)}}{A}=\int dz\left[\frac{L_1}{2}\left[\frac{d\eta}{dz}\right]^2+L_2\left[\frac{d\rho}{dz}\right]\left[\frac{d\eta}{dz}\right]\right] \;, \tag{2.15a}$$

$$\frac{F_{A,\mathrm{NL}}^{(4)}}{A}=\int dz\left[\frac{M_1}{2}\left[\frac{d^2\eta}{dz^2}\right]^2+M_2\left[\frac{d^2\rho}{dz^2}\right]\left[\frac{d^2\eta}{dz^2}\right]\right] \;, \tag{2.15b}$$

where $\eta=\bar{\eta}\rho$. The elastic constants L_1, L_2, M_1, and M_2 are given by

$$L_1=-\pi\int_0^\infty dr\, r^4[g_2(r)+\tfrac{22}{105}g_3(r)+\tfrac{7}{15}g_4(r)] \;, \tag{2.16a}$$

$$L_2=-\frac{4\pi}{15}\int_0^\infty dr\, r^4 g_1(r) \;, \tag{2.16b}$$

$$M_1=\frac{\pi}{20}\int_0^\infty dr\, r^6[g_2(r)+\tfrac{2}{7}g_3(r)+\tfrac{11}{21}g_4(r)] \;, \tag{2.16c}$$

$$M_2=\frac{2\pi}{105}\int_0^\infty dr\, r^6 g_1(r) \;. \tag{2.16d}$$

The above derivation assumes a constant director $\hat{\mathbf{n}}$ along the z axis, and spatial variation of ρ and $\bar{\eta}$ only in this direction. This is appropriate to a mean-field description of the smectic phase. For treatment of fluctuations, one would have to allow for arbitrary spatial variation of ρ, $\bar{\eta}$, and $\hat{\mathbf{n}}$. We shall not consider this extension in the present work, but leave that as an important area for future study.

The mean-field-type expression (2.7) on which the preceding analysis was based is usually considered to be valid only for long-range interaction potentials $V(\mathbf{r}_{12},\omega_1,\omega_2)$. This excludes, in particular, the contributions of short-range repulsive interactions. Generalizations of (2.7) which account for the latter effects can be formulated in terms of the Ornstein-Zernike direct correlation function [12]. The simplest modification of the preceding results suggested by such analyses generalizes the elastic constants B, C, and L_1 to M_2 to become functions of the local density ρ [12(a)]. For simplicity, and also because we find this to be of most relevance (see Secs. III and IV), we shall apply this modification only to the isotropic nonlocal free energy $F_{0,\mathrm{NL}}$. To full quartic order in the density gradient, and assuming spatial variation along the z direction only, this generalizes the earlier expression (2.11) to [12(b)]

$$\begin{aligned} \frac{F_{0,\mathrm{NL}}}{A}=\int dz\Bigg[&\frac{B(\rho)}{2}\left[\frac{d\rho}{dz}\right]^2+\frac{(C(\rho)}{2}\left[\frac{d^2\rho}{dz^2}\right]^2 \\ &+\frac{G(\rho)}{12}\left[\frac{d\rho}{dz}\right]^4\Bigg] \;. \end{aligned} \tag{2.17}$$

Here $B(\rho)$, $C(\rho)$, and $G(\rho)$ are functions of the density ρ, and now contain both the effects of isotropic attractive interactions [as in (2.11)] and density-dependent repulsive effects. We shall approximate these by the phenomenological expressions

$$B(\rho)=B_0+B_1\rho+B_2\rho^2\ , \tag{2.18a}$$

$$C(\rho)=C_0+C_1\rho+C_2\rho^2\ , \tag{2.18b}$$

where B_0 to C_2 are constants. For simplicity we shall set $G=G_0$, thus neglecting any density dependence of this coefficient in (2.17).

To summarize, the Helmholtz free energy is given by Eqs. (2.3)–(2.8), (2.14), (2.15), (2.17), and (2.18), where $F_{\mathrm{NL}}=F_{0,\mathrm{NL}}+F_{A,\mathrm{NL}}$. The fact that F_{NL} is expanded only up to quartic gradient terms limits the applicability of the theory, in principle, to long-wavelength modulations.

B. Method of solution

By defining reduced temperature $t=T/T_c$, and choosing appropriate units for density ρ, order parameter $\bar{\eta}$, and for the various material constants in the free energy derived previously, the latter can be expressed as

$$\frac{F}{A}=\int_{-\infty}^{\infty}dz[f_{0,L}(z)+f_{A,L}(z)+f_{A,\mathrm{NL}}^{(2)}(z)+f_{A,\mathrm{NL}}^{(4)}(z)]\ , \tag{2.19}$$

where

$$f_{0,L}=\frac{(t-1)}{2}(\rho-1)^2+\frac{b}{4}(\rho-1)^4\ , \tag{2.20a}$$

$$f_{A,L}=\beta\rho\left[\frac{(\alpha_1 t+1-\gamma\rho)}{\alpha}\bar{\eta}^2-2\bar{\eta}^3+\bar{\eta}^4\right]\ , \tag{2.20b}$$

$$f_{0,\mathrm{NL}}=\frac{B(\rho)}{2}\left[\frac{d\rho}{dz}\right]^2+\frac{C(\rho)}{2}\left[\frac{d^2\rho}{dz^2}\right]^2+\frac{G_0}{12}\left[\frac{d\rho}{dz}\right]^4\ , \tag{2.20c}$$

$$f_{A,\mathrm{NL}}^{(2)}=\frac{L_1}{2}\left[\frac{d\eta}{dz}\right]^2+L_2\left[\frac{d\rho}{dz}\right]\left[\frac{d\eta}{dz}\right]\ , \tag{2.20d}$$

$$f_{A,\mathrm{NL}}^{(4)}=\frac{M_1}{2}\left[\frac{d^2\eta}{dz^2}\right]^2+M_2\left[\frac{d^2\rho}{dz^2}\right]\left[\frac{d^2\eta}{dz^2}\right]\ , \tag{2.20e}$$

where $\eta=\bar{\eta}\rho$, and $B(\rho)$ and $C(\rho)$ are given by (2.18), with appropriate rescaled coefficients B_0 to C_2.

The theory is analyzed by comparing the free energies of the following phases.

(1) The isotropic (liquid and vapor) phases with

$$\rho=\rho_0,\quad \bar{\eta}=0\ ; \tag{2.21}$$

(2) the nematic phase with

$$\rho=\rho_0,\quad \bar{\eta}=\bar{\eta}_0\ ; \tag{2.22}$$

(3) the smectic phase with

$$\rho=\rho_0+\sum_{m=1}^{M}\rho_m\cos(mqz)\ , \tag{2.23a}$$

$$\bar{\eta}=\bar{\eta}_0+\sum_{m=1}^{M}\bar{\eta}_m\cos(mqz)\ . \tag{2.23b}$$

In these equations M is some appropriately large truncation index, $q=2\pi/d$ where d is the smectic layer spacing, ρ_0 is the average number density, and $\bar{\eta}_0$ is the mean orientational order parameter. Using the definition $\eta=\bar{\eta}\rho$, it follows that

$$\eta=\eta_0+\sum_{m=1}^{2M}\eta_m\cos(mqz)\ , \tag{2.23c}$$

where each η_m can be expressed as a function of $\eta_{m'}$ and $\rho_{m'}$ for $m'\leq m$.

For the uniform (isotropic and nematic) phases, with constant density and order parameter, the total free energy per volume equals $f_{0,L}+f_{A,L}$, where the latter free-energy densities are given by Eqs. (2.20a) and (2.20b). For the smectic phase, characterized by periodicity d, the free energy per volume is evaluated from

$$\frac{F}{V}\equiv f=\frac{1}{d}\int_0^d dz\,f(z)\ , \tag{2.24}$$

using the total free-energy density defined in (2.19) and (2.20). Substituting (2.23) for $\rho(z)$, $\bar{\eta}(z)$, and $\eta(z)$, the integration in (2.24) can be done analytically. At fixed mean density ρ_0 and temperature t, the free energy f is minimized with respect to q, $\bar{\eta}_0$, $\bar{\eta}_m$, and ρ_m using a quasi-Newton method. We have used M as large as 10, although for most purposes of interest it was found that $M=4$ is sufficient. First-order phase coexistence boundaries have been calculated by equating the grand and chemical potentials of the coexisting phases.

C. Landau expansion

When the nematic-smectic phase boundaries are either second order or weakly first order, they can be determined approximately (or exactly when they are second order) by a Landau analysis. This is based on expanding the smectic free energy $f(\rho_1,\rho_2,\ldots;\bar{\eta}_0,\bar{\eta}_1,\bar{\eta}_2,\cdots)$ at fixed ρ_0, t, and period $d=2\pi/q$ about that of a nematic phase characterized by a nonzero value $\bar{\eta}_{0N}$ of only the mean orientational order parameter $\bar{\eta}_0$. On eliminating, by minimization of f, all order parameters $\rho_2,\ldots$, $\bar{\eta}_0-\bar{\eta}_{0N},\bar{\eta}_1,\bar{\eta}_2,\ldots$, in terms of the fundamental Fourier component ρ_1, the Landau expansion reduces to the expected form

$$f-f^N=\alpha_0\rho_1^2+\gamma_0\rho_1^4+o(\rho_1^6)\ , \tag{2.25}$$

where f^N is the free energy per unit volume of the nematic phase. It has been shown in previous works [13,14] on smectic liquid crystals that the coefficient α_0 depends only on coupling between the leading-order Fourier components ρ_1 and $\bar{\eta}$, while γ_0 depends additionally on coupling to the second-order components ρ_2 and $\bar{\eta}_2$ as well as $\bar{\eta}_0-\bar{\eta}_{0N}$. In particular, one finds

$$\alpha_0=\frac{1}{2}\left[\chi_{\rho_1\rho_1}-\frac{\chi_{\rho_1\eta_1}^2}{\chi_{\eta_1\eta_1}}\right]\ , \tag{2.26a}$$

where

$$\chi_{\rho_1\rho_1}=\chi_{\rho\rho}^{(0)}+\frac{Bq^2}{2}+\frac{Cq^4}{2}\ , \tag{2.26b}$$

$$\chi_{\eta_1\eta_1}=\chi_{\eta\eta}^{(0)}+\frac{L_1q^2}{2}+\frac{M_1q^4}{2}\ , \tag{2.26c}$$

$$\chi_{\rho_1\eta_1}=\chi_{\rho\eta}^{(0)}+\frac{L_2q^2}{2}+\frac{M_2q^4}{2}\ , \tag{2.26d}$$

and

$$\begin{aligned}\chi_{\rho\rho}^{(0)}&=\tfrac{1}{2}\left[\frac{\partial^2 f_{0,L}}{\partial\rho_0^2}+\frac{\partial^2 f_{A,L}}{\partial\rho_0^2}\right]\\ &=\tfrac{1}{2}[(t-1)+3(\rho_0-1)^2]\\ &\quad+\frac{\beta\overline{\eta}_{0N}^{\,2}}{\rho_0}\left[\frac{\alpha_1 t+1}{\alpha}-6\overline{\eta}_{0N}+6\overline{\eta}_{0N}^{\,2}\right]\ ,\end{aligned} \tag{2.26e}$$

$$\begin{aligned}\chi_{\eta\eta}^{(0)}&=\tfrac{1}{2}\left[\frac{\partial^2 f_{A,L}}{\partial\eta_0^2}\right]\\ &=\frac{\beta}{\rho_0}\left[\frac{(\alpha_1 t+1-\gamma\rho_0)}{\alpha}-6\overline{\eta}_{0N}+6\overline{\eta}_{0N}^2\right]\ ,\end{aligned} \tag{2.26f}$$

$$\begin{aligned}\chi_{\rho\eta}^{(0)}&=\tfrac{1}{2}\left[\frac{\partial^2 f_{A,L}}{\partial\rho_0\partial\eta_0}\right]\\ &=-\frac{\beta\overline{\eta}_{0N}}{\rho_0}\left[\frac{\alpha_1 t+1}{\alpha}-6\overline{\eta}_{0N}+6\overline{\eta}_{0N}^{\,2}\right]\ ,\end{aligned} \tag{2.26g}$$

and

$$B=B_0+B_1\rho_0+B_2\rho_0^2\ , \tag{2.26h}$$

$$C=C_0+C_1\rho_0+C_2\rho_0^2\ . \tag{2.26i}$$

In the above expressions, $\overline{\eta}_{0N}$ is the equilibrium value of the order parameter in the nematic phase, obtained as a function of ρ_0 and t by minimizing the local anisotropic free energy f_{AL} in (2.20b). The expression for γ_0 is considerably more complex and will not be shown here.

As is well known, (2.25) predicts that a second-order nematic-smectic transition occurs when $\alpha_0=0$, provided that $\gamma_0>0$ as well as all higher-order coefficients being positive. If $\gamma_0<0$, then the vanishing of α_0 describes a supercooling spinodal line for the nematic phase, the true (first-order) transition from nematic to smectic having occurred at some higher temperature where α_0 is still positive. The simultaneous vanishing of α_0 and γ_0 determines the location of the tricritical point separating first-order from second-order nematic-smectic transitions.

To try to obtain explicit insight, we consider a long-wavelength (small q) expansion of α_0; in this case (2.26a) becomes

$$\begin{aligned}\alpha_0=\tfrac{1}{2}&\left[\chi_{\rho\rho}^{(0)}-\frac{(\chi_{\rho\eta}^{(0)})^2}{\chi_{\eta\eta}^{(0)}}\right]+\left[\frac{B}{4}-\frac{L_2}{2}\frac{\chi_{\rho\eta}^{(0)}}{\chi_{\eta\eta}^{(0)}}+\frac{L_1}{4}\left[\frac{\chi_{\rho\eta}^{(0)}}{\chi_{\eta\eta}^{(0)}}\right]^2\right]q^2\\ &+\left[\frac{C}{4}+\frac{M_1}{4}\left[\frac{\chi_{\rho\eta}^{(0)}}{\chi_{\eta\eta}^{(0)}}\right]^2-\frac{M_2}{2}\left[\frac{\chi_{\rho\eta}^{(0)}}{\chi_{\eta\eta}^{(0)}}\right]\right.\\ &\qquad\left.-\frac{[L_2-L_1(\chi_{\rho\eta}^{(0)}/\chi_{\eta\eta}^{(0)})]^2}{8\chi_{\eta\eta}^{(0)}}\right]q^4+\cdots\ .\end{aligned} \tag{2.27}$$

We note that $\chi_{\eta\eta}^{(0)}$ is necessarily positive for the existence of a stable nematic phase. Inspection of (2.26e)–(2.26g) then shows that $\chi_{\rho\rho}^{(0)}>0$ and $\chi_{\rho\eta}^{(0)}<0$. The function $[\chi_{\rho\rho}^{(0)}-(\chi_{\rho\eta}^{(0)})^2/\chi_{\eta\eta}^{(0)}]$ is also required to be positive in order that the nematic free energy be a concave function of density ρ_0. The occurrence of a minimum in $\alpha_0(q)$ at non-zero q then requires, in (2.27),

$$\text{coefficient of } q^2<0\ , \tag{2.27a}$$

$$\text{coefficient of } q^4>0\ . \tag{2.27b}$$

It is necessary that the elastic constant L_1 be positive for the stability of the nematic phase. This is established by examining the stability of the nematic phase with respect to inhomogeneity in the nematic director, which has been examined in previous works [15]. For now, we shall also assume that $B,C>0$. Under these conditions, the only way to satisfy condition (2.27a) above is if the elastic constant $L_2<0$. Since L_2 is the coefficient of the term $(d\rho/dz)(d\eta/dz)$ in (2.20d), $L_2<0$ is consistent with the hypothesis that it is the coupling between the modulations in density and orientational order parameter that drives smectic formation.

Condition (2.27b) is favored by having positive values of the elastic constants C, M_1, and M_2, although the last term involving L_1 and L_2 could lead to a violation of that condition. In this case, analysis based on a small-q expansion of α_0 breaks down.

The variables B and C, as given by (2.26h) and (2.26i), are functions of ρ_0. In the above stability analysis we have assumed that they are positive. In obtaining the phase diagram, we shall use B and C to manipulate the shape of the second-order nematic-smectic transition line. This means that some of the constants B_0,B_1,B_2, and C_0,C_1,C_2 may have negative values. This raises the possibility for the existence of a plastic crystal phase which is a one-dimensionally modulated phase with no orientational order ($\overline{\eta}\approx 0$).

Although the analysis in this section suggests the appropriate signs for the phenomenological constants, it does not give numerical values. An estimate of these values can be made by considering specific microscopic models [16].

III. RESULTS

We first summarize the results of the Landau expansion for a second-order nematic-smectic transition. For all results reported in the following, we use $b=1$ (this gives a zero-temperature isotropic liquid-vapor coexistence at $\rho_0=0$ and 2), $\alpha=0.292\,235\,8$, $\alpha_1=0.4$, $\beta=0.01$, and $\gamma=0.608\,311$. We vary the phenomenological constants associated with the nonlocal part of the free energy $f_{\rm NL}$. In particular B_0,B_1,B_2, and C_0,C_1,C_2 are used to manipulate the shape of the second-order lines, which is expected to be similar to that obtained by Mederos and Sullivan [5]. Figure 1 shows the second-order line for $B_0=1$, $B_1=1.5$, $B_2=-1.64$, $C_0=0.368$, $C_1=-0.223$, $C_2=0.25$, $L_1=0.028$, $M_1=0$, $M_2=0$, $G_0=0$, and L_2 varying from -0.15 to -0.08. The second-order line is superimposed on the vapor-nematic-isotropic phase dia-

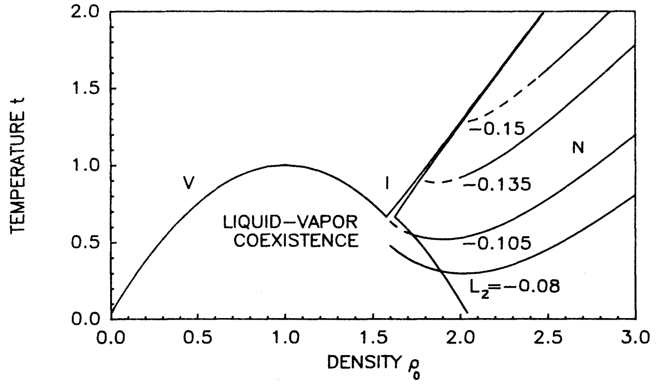

FIG. 1. Nematic-smectic second-order lines superimposed on the vapor(V)-isotropic liquid(I)-nematic(N) phase diagram in the temperature-density plane. Here L_2 varies from -0.08 to -0.15, and other parameters are as given in the text.

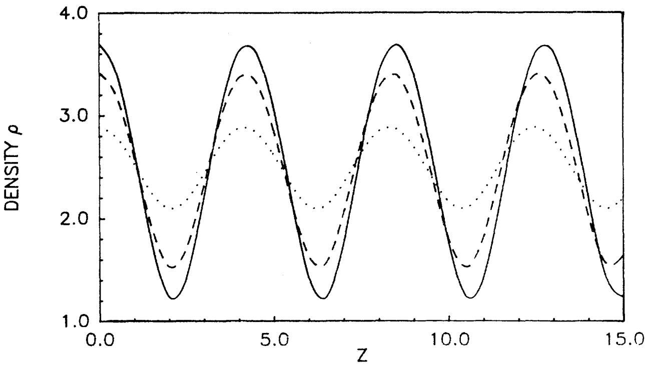

FIG. 3. Plots of the density ρ vs z at $\rho_0=2.5$, $L_2=-0.15$, and $t=0.5$ (solid), $t=1.0$ (dashed), $t=1.62$ (dotted).

gram which was obtained by using the local part of the free energy f_L only. The solid parts of the curves indicate a true second-order transition ($\gamma_0>0$), while the dashed parts indicate a supercooling spinodal line ($\gamma_0<0$). As can be seen, the smectic phase is more prominent for large $|L_2|$, decreasing in range of stability as $|L_2|$ decreases. We have neglected $f^{(4)}_{A,\mathrm{NL}}$ (i.e., have taken $M_1,M_2=0$), since this term is not necessary to induce a smectic phase. The term G_0 does not appear in the Landau coefficient α_0, hence it does not affect the shape of the second-order line. However, G_0 does occur in the Landau coefficient γ_0. Its effect is to increase γ_0, hence extending the range of the second-order nematic-smectic transition and increasing the tricritical density and temperature. We shall keep $G_0=0$ for all subsequent calculations.

Let us now turn to the predictions of the full model. We first do a temperature-density scan to find regions where the smectic phase is stable. For computational convenience, $M=4$ terms in the Fourier series (2.23) are used. This seems sufficient since ρ_m and $\bar{\eta}_m$ (and η_m) decrease rapidly with m. Selected checks using a larger number ($M=10$) of Fourier components show that the results differ negligibly. Plots of $\bar{\eta}$ and ρ as functions of z, the direction of modulation, are given in Figs. 2–5. In Figs. 2 and 3,$L_2=-0.15$ and $\rho_0=2.5$, while t is varied. We can see that the deviation of $\bar{\eta}$ and ρ from their mean values of $\bar{\eta}_0$ and ρ_0 are large ($\bar{\eta}_1$ and ρ_1 larger or comparable to $\bar{\eta}_0$ and ρ_0) far away from the nematic-smectic first-order transition ($t=0.5$ and 1.0), and are small ($\bar{\eta}_1$ and ρ_1 substantially smaller than $\bar{\eta}_0$ and ρ_0) near the transition ($t=1.62$). Figures 4 and 5 give analogous plots for $L_2=-0.08$. Here the deviations of $\bar{\eta}$ and ρ from their mean values are small and decrease as the nematic-smectic second-order phase boundary is approached.

The full temperature-density phase diagrams are given in Figs. 6 ($L_2=-0.15$) and 7 ($L_2=-0.08$). For $L_2=-0.15$, the nematic-smectic phase boundary is first order below $\rho_0=2.56$ (solid) and second order above $\rho_0=2.56$ (dashed). The extension of the second-order line below $\rho_0=2.56$ is a supercooling spinodal line. The Landau expansion, discussed in Sec. II C, predicts a smaller tricritical density $\rho_{\mathrm{critical}}=2.46$. For this system a numerical analysis shows that this is due to the fact that the ρ_1^6 coefficient in the free energy expansion in (2.25) is negative. Note that the density gap for the nematic-smectic coexistence is very small, much smaller than that found by Mederos and Sullivan [5]. This may be due to several *ad hoc* modifications made in deriving our theory. For

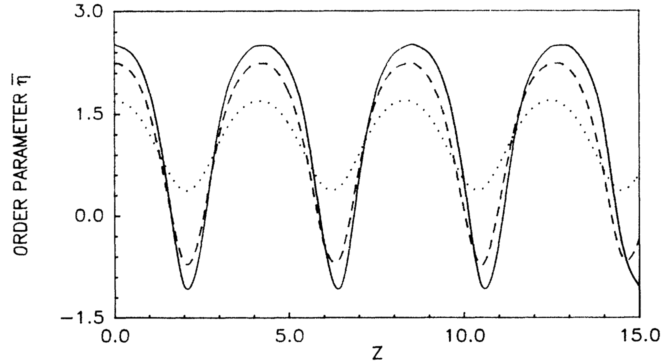

FIG. 2. Plots of the order parameter $\bar{\eta}$ vs z at $\rho_0=2.5$, $L_2=-0.15$, and $t=0.5$ (solid), $t=1.0$ (dashed), and $t=1.62$ (dotted).

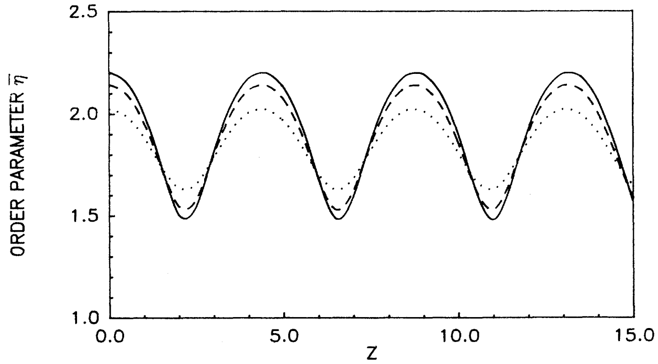

FIG. 4. Plots of the order parameter $\bar{\eta}$ vs z at $\rho_0=2.5$, $L_2=0.08$, and $t=0.1$ (solid), $t=0.2$ (dashed), $t=0.35$ (dotted).

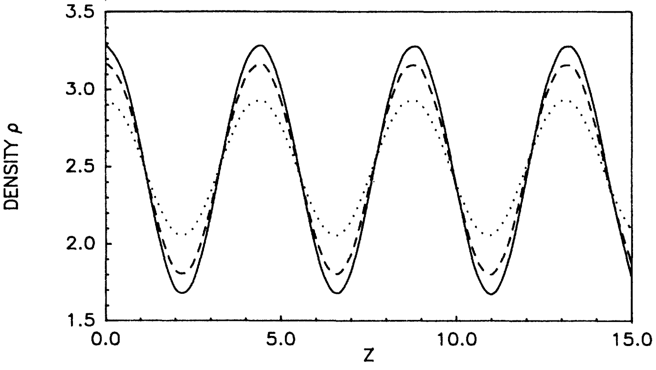

FIG. 5. Plots of the density ρ vs z at $\rho_0=2.5$, $L_2=-0.08$, and $t=0.1$ (solid), $t=0.2$ (dashed), $t=0.35$ (dotted).

$L_2=-0.08$ the nematic-smectic phase boundary is entirely second order, as is predicted by the Landau expansion.

At $L_2=-0.08$ there is a nematic-isotropic liquid-vapor triple point at $t=\frac{2}{3}$ and a critical end point (smectic-nematic-vapor) at $t=0.305$. At $L_2=-0.15$ there are two triple points, smectic-isotropic liquid-vapor at $t=0.82$, and smectic-nematic-isotropic at $t=1.35$. As far as we are aware, none of these phase transitions involving vapor has been directly observed in experiments. Experiments on liquid crystals are usually performed under a fixed atmospheric pressure, although there are several exceptions [17–19]. We know of only one instance where a pressure-induced smectic-nematic-isotropic triple point in a pure compound has been observed [19], although this phenomenon should not be uncommon. Data given by Shashidar and Venkatesh [18] suggest that such a triple point may occur in the cyanobiphenal series *nCB* for $n \geq 9$.

We have not examined the stability of the smectic phase with respect to three-dimensional crystallization. We expect the solid phase to preempt much of the phase domain in Figs. 6 and 7.

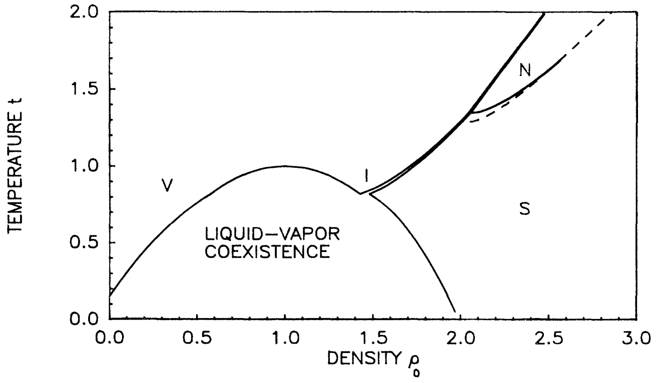

FIG. 6. Full temperature-density phase diagram at $L_2=-0.15$, including the smectic(*S*) phase.

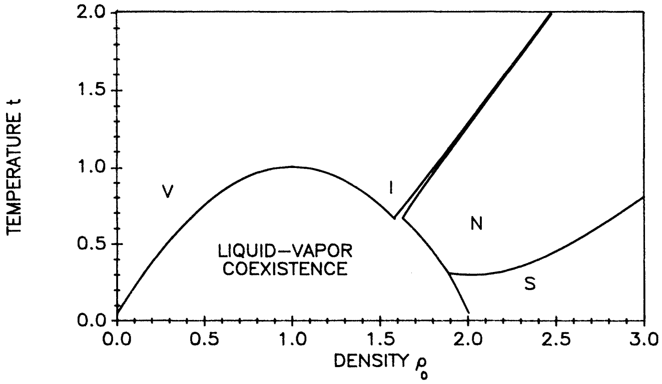

FIG. 7. Full temperature-density diagram at $L_2=-0.08$, including the smectic(*S*) phase.

Another feature of interest is the behavior of the equilibrium smectic period $d=2\pi/q$, where q is the equilibrium smectic wave number. As expected, this is always a decreasing function of the mean density ρ_0, as is shown in Fig. 8. On the other hand, at fixed density the period decreases with increasing temperature, as is observed in Fig. 9. This behavior was also found in Ref. [5]. Such a tendency has indeed been observed experimentally [20] and previously ascribed to increasing orientational disorder with increasing temperature.

We close this section by discussing the possibility for the existence of a plastic crystal, i.e., a one-dimensionally modulated phase with no orientational order. From Fig. 1 one can see that a nematic-smectic second-order line with a sufficiently large slope will intersect the isotropic-nematic transition line and hence lead to a plastic crystal phase at high density. By analyzing the long-wavelength expansion of the coefficient α_0 [Eq. (2.27)], we find that this should occur if $B_2^2-12C_2>0$. Figure 10 shows the second-order line for $B_0=1$, $B_1=1.5$, $B_2=-1.45$, $C_0=0.368$, $C_1=-1.81$, $C_2=0.15$, $L_1=0.04$, and $L_2=-0.16$ superimposed on the nematic-isotropic phase diagram. As can be seen, the second-order line will eventually intersect the nematic-isotropic coexistence curve giving rise to a plastic crystal phase. In connection with earlier remarks in this section, however, such a transition is probably unstable relative to three-dimensional crystal formation.

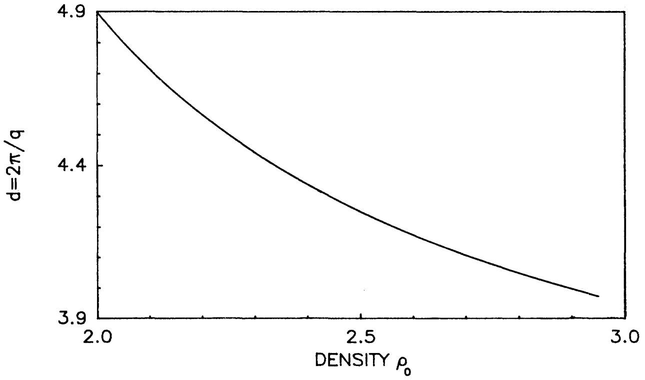

FIG. 8. Variation of the equilibrium smectic period $d=2\pi/q$ with mean density ρ_0, at constant temperature $t=0.5$ and $L_2=-0.15$.

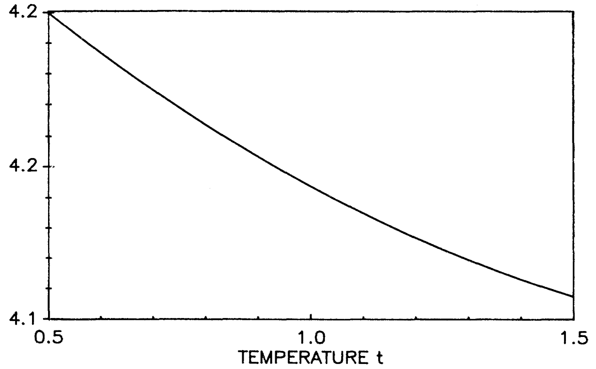

FIG. 9. Variation of the equilibrium smectic period $d = 2\pi/q$ with temperature t, at mean density $\rho_0 = 2.5$ and $L_2 = -0.15$.

IV. DISCUSSION

The results above fulfill the main objective of this paper, namely to demonstrate that a properly formulated Landau–de Gennes theory can self-consistently predict the formation of the smectic phase. A key result of the work is that stability of the smectic phase is primarily determined by the elastic constant L_2, as anticipated in Sec. II C and demonstrated in Fig. 1. Recall that L_2 is the coefficient of the term $(d\rho/dz)(d\eta/dz)$ in the nonlocal free energy $f_{A,\mathrm{NL}}$ [see Eq. (2.20d)], and so the results support our claim that the formation of a smectic phase is due to coupling between gradients of the density and orientational order parameters. In microscopic terms, the constant L_2 is related to the potential $g_1(r_{12})$ [see (2.12) and (2.16b) as well as the potential $V_3(r_{12})$ in Mederos and Sullivan [5]], which couples the relative orientation of the molecular axes and the intermolecular vector $\mathbf{r}_{12}$ and favors side-by-side alignment of parallel rodlike molecules.

Our work also indicates that density-dependent isotropic elastic constants $B(\rho)$ and $C(\rho)$ in the nonlocal free energy $f_{0,\mathrm{NL}}$, which are related to short-range repulsive interactions, are necessary for the formation of a smectic phase, although we have not presented extensive data on this point. Basically, if B and C are kept constant, independent of density, it is found that the temperature along the nematic-smectic phase boundary is always a decreasing function of the mean number density ρ_0, which we consider to be unphysical behavior. This is mainly attributed to the local isotropic free energy $f_{0,L}$, which is an increasing function of density [see (2.20a)] and hence tends to destabilize the smectic at high density. In general, the results obtained here are qualitatively consistent with those from the theory of Mederos and Sullivan [5], on which the present theory was largely based.

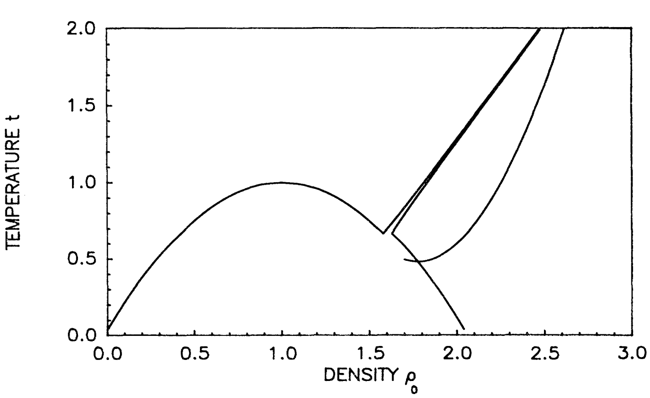

FIG. 10. Plot of the nematic-smectic second-order line for the parameters $\alpha = 0.292\,235\,8$, $\alpha_1 = 0.4$, $\beta = 0.01$, $\gamma = 0.608\,311$, $B_0 = 1$, $B_1 = 1.5$, $B_2 = -1.45$, $C_0 = 0.368$, $C_1 = -1.81$, $C_2 = 0.15$, $L_1 = 0.04$, and $L_2 = -0.16$, superimposed on the vapor-isotropic-nematic phase diagram.

The importance of coupling between density or translational and orientational order in smectic liquid crystals was first pointed out by de Gennes [1,4]. Two aspects of this coupling have usually been emphasized, namely (i) determining the order of the nematic-smectic transition, and (ii) specifying the layer direction in the smectic phase. What has not previously been demonstrated, however, is how such coupling is necessary to drive smectic formation in the first place, which has been the focus of this work. Contributions relevant to aspect (i) above are contained in the quartic Landau coefficient γ_0 defined in (2.25).

Aspect (ii) above is related to the elastic energy for distortion of the smectic layers introduced by de Gennes [1,4]. A full analysis of this effect in the present context requires generalizing this work to the treatment of fluctuation effects. This, in turn, requires generalizing the derivation of the gradient terms in the free energy to allow for arbitrary spatial variation of $\rho(\mathbf{r})$, $\overline{\eta}(\mathbf{r})$, and the director $\hat{\mathbf{n}}(\mathbf{r})$. While an analysis of the resulting theory is not expected to be easy, a feasible initial aim should be to obtain a generalization of the Ldg free energy in Eq. (1.1) exhibiting rotation-translation coupling effects that are possibly "hidden" in the latter expression. Conceivably, this study could reveal new types of fluctuation terms which are relevant to continuous nematic-smectic phase transitions.

The type of translational-orientational coupling discussed here has also been found essential for the occurrence of surface-induced ordering and of preferred molecular orientations [21] at liquid-vapor and nematic-isotropic interfaces of nematic liquid crystals [10,22–24]. An important extension of this work is to the treatment of such interfacial phenomena when smectic phases are involved. We note that previous studies [25,26] of smectic ordering at liquid-vapor interfaces have modeled the interface using an inpenetrable wall in place of the coexisting vapor. The present theory, in principle, allows for the occurrence of a diffuse liquid-vapor interface characterized by continuous variation in the density and orientational order parameter.

ACKNOWLEDGMENT

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