

Landau-Ginzburg mean-field theory for the nematic to smectic-C and nematic to smectic-A phase transitions*

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A Landau-Ginzburg free energy is presented that yields a nematic to smectic-A (NA) transition, a nematic to smectic-C (NC) transition, and a Lifshitz point (at the boundary between the NA and NC transitions). Fluctuation enhancements of the Frank elastic constants are calculated. For the NC transition, all three elastic constants K_1 , K_2 , and K_3 diverge as ξ^2 , where ξ is the correlation length for fluctuations of the smectic order parameter. At the Lifshitz point, K_1 and K_2 diverge as $\ln\xi$ whereas K_3 diverges as ξ .

I. INTRODUCTION

In the nematic liquid crystalline state, long bar molecules are oriented on the average with their long axes along a preferred direction specified by a unit vector \hat{n} , called the director.^{1,2} The molecular centers of mass are, however, free to diffuse throughout the system so that translational invariance is not destroyed. The nematic state is shown schematically in Fig. 1(a). In the smectic-A phase [shown in Fig. 1(b)] the molecules segregate into two-dimensional planes while maintaining translational invariance along the planes. In the smectic-C phase [shown in Fig. 1(c)] the molecules are tilted at an angle θ to the normal to the smectic planes. Phase transitions between all of these phases are possible. The nematic to smectic-A (NA) transition has been the most studied.³⁻¹⁰ If director fluctuations are ignored, it can be a second-order transition with helium exponents.³⁻⁶ Theoretical considerations indicate that director fluctuations cause the transition to be first order.^{11,12} Though specific-heat and volumetric measurements¹⁰ indicate a first-order transition, careful light scattering experiments⁹ show no indication of a first-order transition. The smectic-A to smectic-C (AC) transition can be second order^{6,13-15} and is believed to have helium exponents.⁶ There can also be a direct nematic to smectic-C (NC) transition.^{6,16} This has been the least studied of the transitions. In this paper, we present and study a model which has the potential to include all of these transitions. For compactness, we will refer to this as the nematic-smectic-A-smectic-C (NAC) model.

Our starting point will be the observation that the x-ray scattering in the nematic phase (single crystal) in the vicinity of the NA transition shows strong peaks at wave number $\vec{q}_A = \pm q_0 \hat{n}$,^{6,17} shown in Fig. 2(a). Near an NC transition, these two

peaks spread out into two rings at $\vec{q}_c = (\pm q_{\parallel}, q_{\perp} \cos\varphi, q_{\perp} \sin\varphi)$,^{6,18} shown in Fig. 2(b). The latter observation prompted de Gennes⁶ to introduce an infinite-dimensional order parameter $\Psi_{\varphi} = \rho(q_{\parallel}, q_{\perp} \cos\varphi, q_{\perp} \sin\varphi)$ for the smectic-C state where ρ is the center-of-mass density. In our model the NA and NC transitions can be described by the same free energy with different parameters. For the NA transition, the free energy is minimized if the center-of-mass density is periodic with wave number $\pm q_0 \hat{n}$; for the NC transition, it is minimized if the center-of-mass density is periodic with wave number \vec{q}_c . The de Gennes and NAC models, though motivated by the same observation, predict different behavior. In particular, near the NC transition the de Gennes theory predicts that the Frank elastic constants⁶ K_1 , K_2 , and K_3 diverge as $\xi^{2/3}$, where ξ is the correlation length, while the NAC theory predicts that all three elastic constants diverge as ξ^2 .

Models similar to the NAC model have appeared in other contexts. In particular, the NAC model is very similar to those used to describe transitions from the paramagnetic state to helical spin states^{19,20} and to that used to describe the Benard instability in a cylindrical cavity.²¹ All of these models have the common feature that fluctuations are a maximum at wave numbers $|\vec{q}_{\perp}| = q_c$, where \vec{q}_{\perp} is an m -dimensional vector in a d -dimensional space. Mean-field theory predicts a second-order transition for these models. Fluctuations, however, are believed to lead to a first-order transition when $m = d$ or $m = d - 1$.^{20,21} The NC transition has $d = 3$ and $m = 2$ so the transition is expected to be first order.²¹ Nevertheless, pretransitional effects can be important, and the mean-field calculations presented in this paper are expected to be valid in some temperature range above the first-order transition. It is unclear whether a crossover from mean-field be-

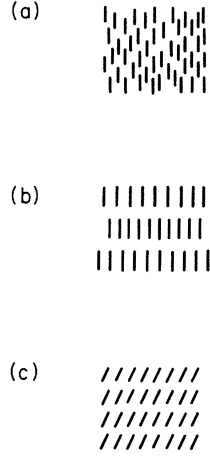


FIG. 1. Schematic representation of the position and orientation of molecules in (a) the nematic liquid phase, (b) the smectic-A phase, and (c) the smectic-C phase.

havior to some quasicritical behavior will occur before the first-order transition occurs. To date there is no satisfactory renormalization treatment of this model showing fixed points with first-order runaways. The boundary between the NA and NC transitions is a special point representative of a class of transitions recently considered by Hornreich, Luban, and Shtrikman.²² This transition is second order with anisotropic scaling and can be treated using the renormalization group.

Section II introduces the model and Sec. III presents perturbation calculations of the elastic constants for the NA and NC transitions and at the Lifshitz point.

II. THE MODEL

In the smectic phases, the center-of-mass density $\rho(\vec{r})$ becomes periodic with fundamental wave number $\vec{q}_0 = (\pm q_{||}, \vec{q}_{\perp})$ ($q_{\perp} = 0$ in the smectic-A phase). We will, therefore, take the part of ρ with wave numbers in the vicinity of \vec{q}_0 to be the order parameter $m(\vec{r})$ of our theory:

$$m(\vec{r}) = \int_D \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot\vec{r}} \rho(\vec{k}), \quad (2.1)$$

where $\rho(\vec{k})$ is the Fourier transform of $\rho(\vec{r})$ and D is a two-part domain (excluding $\vec{k} = 0$) centered around $(\pm q_{||}, 0, 0)$ and large enough to contain the circles $k_{||} = \pm q_{||}$, $|k_{\perp}| = |\vec{q}_{\perp}|$. The model Landau-Ginzburg Hamiltonian can be written as a sum of three parts

$$\beta H = \beta H_m + \beta H_{e1} + \beta H_4, \quad (2.2)$$

where $\beta = 1/kT$. H_m contains terms up to second order in the order parameter:

$$\beta H_m = \frac{1}{2} \int d^3r \left(am^2 + D_{||} [(\vec{n} \cdot \nabla)^2 m]^2 - C_{||} (\vec{n} \cdot \nabla m)^2 + \frac{C_{\perp}^2}{4D_{||}} m^2 + C_{\perp} \delta_{ij}^T \nabla_i m \nabla_j m + D_{\perp} (\nabla_{\perp}^2 m)^2 \right), \quad (2.3)$$

where \vec{n} is the nematic director which may vary in space. The summation convention on repeated Cartesian indices is understood, $\delta_{ij}^T = \delta_{ij} - n_i n_j$ is the projection operator onto directions perpendicular to \vec{n} , and $\nabla_{\perp}^2 = \delta_{ij}^T \nabla_i \nabla_j$. $a = a'[(T - T_{NA})/T_{NA}]$ changes sign at the NA transition temperature T_{NA} . H_{e1} is the Frank free energy^{1,2} for distortions in the nematic director:

$$\beta H_{e1} = \frac{\beta}{2} \int d^3r \{ K_1^0 (\nabla \cdot \vec{n})^2 + K_2^0 [\vec{n} \cdot (\nabla \times \vec{n})]^2 + K_3^0 [\vec{n} \times (\nabla \times \vec{n})]^2 \}, \quad (2.4)$$

where K_1^0 , K_2^0 , and K_3^0 are the unrenormalized Frank elastic constants. H_4 is the fourth-order term needed to stabilize the ordered phase:

$$\beta H_4 = u \int d^3r m^4(r). \quad (2.5)$$

The partition function for this model is calculated in the usual way by taking the functional integral of $e^{-\beta H}$ over all configurations of $n_i(r)$ and $m(r)$:

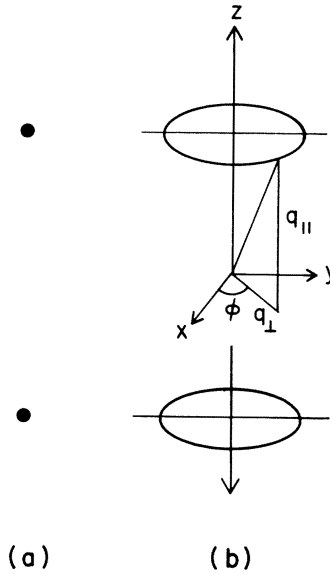


FIG. 2. X-ray intensity. Region of maximum x-ray scattering intensity in the vicinity of (a) the nematic to smectic-A transition and (b) the nematic to smectic-C transition.

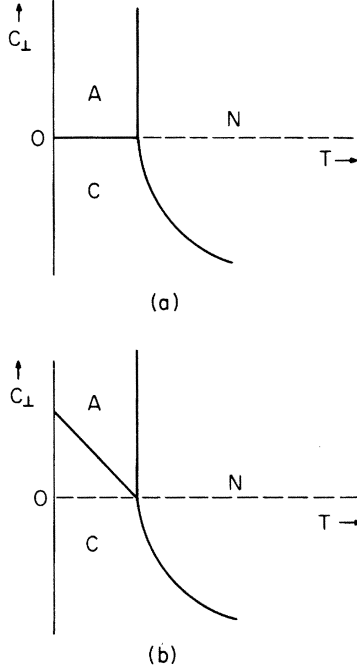


FIG. 3. (a) Phase diagram for the NAC model showing nematic (N), smectic-A (A) and smectic-C (C) phases. (b) Phase diagram for the modified NAC model presented in Appendix A.

$$Z = \int \mathfrak{D}n_i(r) \mathfrak{D}m(r) e^{-\beta H}. \quad (2.6)$$

In the nematic phase, H_4 can be neglected in the mean-field theory, this leads to an x-ray intensity in the vicinity of \vec{q}_0 of

$$I(k) \sim \langle \rho(k) \rho(-k) \rangle \equiv \langle m(k) m(-k) \rangle = \frac{1}{\bar{a} + D_{\parallel}(k_{\parallel}^2 - q_{\parallel}^2)^2 + C_{\perp} k_{\perp}^2 + D_{\perp} k_{\perp}^4}, \quad (2.7)$$

where $q_{\parallel}^2 = C_{\parallel}/2D_{\parallel}$. When $C_{\perp} > 0$, $I(k)$ has peaks at $k_{\parallel} = \pm q_{\parallel}$ corresponding to fluctuations into the smectic-A phase. When C_{\perp} is negative Eq. (2.7) can be rewritten

$$I(k) \sim \frac{1}{\bar{a} + D_{\parallel}(k_{\parallel}^2 - q_{\parallel}^2)^2 + D_{\perp}(k_{\perp}^2 - q_{\perp}^2)^2}, \quad (2.8)$$

where $q_{\perp}^2 = |C_{\perp}|/2D_{\perp}$ and

$$\begin{aligned} \bar{a} &= a'(T - T_{\text{NC}})/T_{\text{NA}}, \\ T_{\text{NC}} &= T_{\text{NA}} + C_{\perp}^2 T_{\text{NA}}/4D_{\perp} a'. \end{aligned} \quad (2.9)$$

Thus for $C_{\perp} < 0$, $I(k)$ is a maximum on the two rings $(\pm q_{\parallel}, q_{\perp} \cos \varphi, q_{\perp} \sin \varphi)$ as required in the vicinity of the NC transition [cf., Fig. 2(b)]. Correlations in the directions parallel to \vec{n} die off

with a correlation length

$$\xi_{\parallel}^2 = \begin{cases} 2C_{\parallel}/a' \sim (T - T_{\text{NA}})^{-1} & \text{if } C_{\perp} > 0, \\ 2C_{\parallel}/a' \sim (T - T_{\text{NC}})^{-1} & \text{if } C_{\perp} < 0. \end{cases} \quad (2.10)$$

and correlations in directions perpendicular to \vec{n} die off with length

$$\xi_{\perp}^2 = \begin{cases} C_{\perp}/a' \sim (T - T_{\text{NA}})^{-1} & \text{if } C_{\perp} > 0, \\ 2|C_{\perp}|/a' \sim (T - T_{\text{NC}})^{-1} & \text{if } C_{\perp} < 0. \end{cases} \quad (2.11)$$

Equations (2.8), (2.9), and (2.11) yield the usual mean-field critical exponents $\gamma = 1$ and $\nu = \frac{1}{2}$. Equation (2.2) can also be minimized in the ordered phase in the usual way. The resulting phase diagram is shown in Fig. 3(a).

The model presented here does not show a smectic-A to smectic-C transition as a function of temperature. Such a transition is easily produced as shown in Appendix A by adding a term proportional to

$$\int m^2(r) \vec{\nabla}_{\perp} m(r) \cdot \vec{\nabla}_{\perp} m(r) d^3r.$$

Addition of this term, however, does not affect the elastic constant calculations presented in Sec. III.

Equation (2.2) reduces when $C_{\perp} > 0$ to the model introduced by de Gennes^{5,6} to describe the nematic to smectic-A transition

$$\begin{aligned} \beta H_0 &= \int d^3r \left(A |\psi|^2 + \frac{1}{2M_v} |\nabla_{\parallel} \psi|^2 \right. \\ &\quad \left. + \frac{1}{2M_T} |(\vec{\nabla}_{\perp} - q_{\parallel} \delta \vec{n}) \psi|^2 \right), \\ \beta H_4 &= \frac{3}{2} u \int |\psi|^4, \end{aligned} \quad (2.12)$$

where $\delta \vec{n}$ is the deviation of \vec{n} from its uniform equilibrium direction,

$$m(\vec{r}) = (2)^{-1/2} [e^{i q_{\parallel} z} \psi(r) + e^{-i q_{\parallel} z} \psi^*(r)], \quad (2.13)$$

where $z = \vec{n} \cdot \vec{r}$ and

$$A = \frac{1}{2} a, \quad C_{\perp} = 1/M_T, \quad C_{\parallel} = 1/2M_v. \quad (2.14)$$

III. ELASTIC CONSTANTS

In the smectic-A phase, bend and twist distortions of the director, even of small wave number, create large separations of the smectic planes. Thus these distortions have a finite rather than a vanishing energy at zero wave number in the A phase. Above T_{NA} , fluctuations into the A phase will, therefore, cause K_2 and K_3 to grow and finally diverge at T_{NA} . Splay deformations on the other hand have energy going to zero with wave number, even in the A phase. Therefore, no divergent anomalies are expected at T_{NA} . Calculations by

de Gennes⁶ and by Jähnig and Brochard,²³ in fact, predict that K_2 and K_3 diverge as the correlation length ξ and that K_1 undergoes no violent change at T_{NA} . A number of experiments^{8,9} have verified that K_2 and K_3 diverge and that K_1 is relatively well behaved at T_{NA} , though agreement on the critical exponents for ξ has not been reached. In the smectic-C phase, all three director distortions lead to large separations of the smectic planes. One would, therefore, expect K_1 , K_2 , and K_3 to diverge near T_{NC} . There is some experimental evidence that this is the case.¹⁶ The de Gennes theory⁶ of the NC transition predicts that K_1 , K_2 , and K_3 diverge as $\xi^{3/2}$. The theory we present here predicts that all three will diverge as ξ^2 in three dimensions.

Our calculations are a straightforward perturbation expansion in the director-order-parameter couplings. In equilibrium, the director is uniform in space: $\vec{n}(r) = \vec{n}^0$. For convenience, we will take \vec{n}^0 (a unit vector) to point along the third axis. Deviations from equilibrium are expressed in terms of

$$\begin{aligned} \delta\vec{n} &= (\delta n_1, \delta n_2, \{1 - [(\delta n_1)^2 + (\delta n_2)^2]\}^{1/2} - 1) \\ &\cong (\delta n_1, \delta n_2, -\frac{1}{2}[(\delta n_1)^2 + (\delta n_2)^2]). \end{aligned} \quad (3.1)$$

We can now expand βH_m in powers of $\delta\vec{n}$:

$$\beta H_m = \beta H_0 + \beta H_1 + \beta H_2 + O((\delta n)^3), \quad (3.2)$$

where βH_0 is given by Eq. (2.3) with \vec{n} replaced by \vec{n}^0 and

$$\beta H_1 = \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} \Gamma_i(\vec{k}, \vec{q}) n_i(-\vec{k}) m(-\vec{q}) m(\vec{q} + \vec{k}), \quad (3.3)$$

$$\begin{aligned} \beta H_2 &= \int \frac{d^3k_1}{(2\pi)^3} \int \frac{d^3k_2}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} \Gamma_{ij}^{(2)}(\vec{k}_1, \vec{k}_2, \vec{q}) \\ &\quad \times n_i(-\vec{k}_1) n_j(-\vec{k}_2) \\ &\quad \times m(\vec{q}) m(-\vec{q} + \vec{k}_1 + \vec{k}_2), \end{aligned} \quad (3.4)$$

where

$$\begin{aligned} \Gamma_i(\vec{k}, \vec{q}) &= D_{ii} [q_i q_{ii} (\vec{q} + \vec{k})_{ii}^2 + (\vec{q} + \vec{k})_i (\vec{q} + \vec{k})_{ii} q_{ii}^2] \\ &\quad - \frac{1}{2} (C_{ii} + C_{\perp}) (2q_i q_{ii} + q_i k_{ii} + q_{ii} k_i) \\ &\quad - D_{\perp} [q_i q_{ii} (\vec{q} + \vec{k})_i^2 + (\vec{q} + \vec{k})_i (\vec{q} + \vec{k})_{ii} q_{ii}^2]. \end{aligned} \quad (3.5)$$

The expression for $\Gamma_{ij}^{(2)}$ is rather complicated. Since it will not be used directly in any calculations, we will not reproduce it here.

We now introduce propagators for the order parameter and the director:

$$G(\vec{k}) = \langle m(\vec{k}) m(-\vec{k}) \rangle,$$

$$D_{ij}(\vec{k}) = \langle \delta n_i(\vec{k}) \delta n_j(-\vec{k}) \rangle.$$

When H_m is replaced by H_0 , $G(k)$ reduces to $G^0(k)$ given by Eq. (2.7). $D_{ij}(\vec{k})$ has two independent components. If \vec{k} is chosen to be in the 1-3 plane and the coupling to m is ignored, they are

$$D_{11}^0(\vec{k}) = \frac{1}{\beta (K_1^0 k_1^2 + K_3^0 k_3^2)}, \quad (3.5a)$$

$$D_{22}^0(\vec{k}) = \frac{1}{\beta (K_2^0 k_1^2 + K_3^0 k_3^2)}. \quad (3.5b)$$

When the coupling to m is included, D_{ij} satisfies Dyson's equation $D_{ij}^{-1}(\vec{k}) = (D_{ij}^0)^{-1}(\vec{k}) - \pi_{ij}(\vec{k})$. The long-wavelength forms of D_{11} and D_{22} are the same as in Eqs. (3.5) with K_1^0 , K_2^0 , and K_3^0 replaced by the renormalized elastic constants K_1 , K_2 , and K_3 . The lowest-order diagrams for $\pi_{ij}(\vec{k})$ are shown in Fig. 4. In Appendix B, we derive a Ward identity which shows that Fig. 4(b) exactly cancels the zero-momentum part of Fig. 4(a). The diagrams in Fig. 4, therefore, yield

$$\begin{aligned} \pi_{ij}(k) &= -2 \int \frac{d^3q}{(2\pi)^3} \{ \Gamma_i(\vec{k}, \vec{q}) \Gamma_j(\vec{k}, \vec{q}) G^0(\vec{q}) G^0(\vec{q} + \vec{k}) \\ &\quad - \Gamma_i(\vec{0}, \vec{q}) \Gamma_j(\vec{0}, \vec{q}) [G^0(\vec{q})]^2 \}. \end{aligned} \quad (3.6)$$

This is in fact the most divergent contribution to π_{ij} when a (or \bar{a}) goes to zero.

Evaluating Eq. (3.6) we obtain the elastic constant enhancement near the NA and NC transitions and near the Lifshitz point.

A. NA transition

$$\begin{aligned} \delta K_2 &= \frac{kT}{24\pi} q_{ii}^2 \frac{C_{\perp}}{(2C_{ii}a)^{1/2}} = \frac{kT}{24\pi} q_{ii}^2 \frac{\xi_{\perp}^2}{\xi_{ii}}, \\ \delta K_3 &= \frac{kT}{24\pi} q_{ii}^2 \left(\frac{2C_{ii}}{a} \right)^{1/2} = \frac{kT}{24\pi} q_{ii}^2 \xi_{ii}. \end{aligned} \quad (3.7)$$

There are no divergent contributions to K_1 as ex-

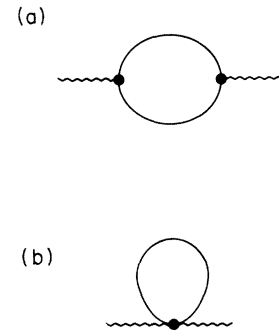


FIG. 4. Diagrams contributing to the fluctuation enhancement of the Frank elastic constants.

pected. Equations (3.7) are in agreement with the calculation of de Gennes^{5,6} as corrected by Jähnig and Brochard.²³

B. NC transition

$$\begin{aligned}\delta K_1 &= \frac{9kT}{64\pi} \frac{q_{\parallel}}{(D_{\parallel}D_{\perp})^{1/2}} \frac{|C_{\perp}|^2}{\bar{a}} \left(1 + \frac{D_{\parallel}}{D_{\perp}} \frac{2}{9}\right) \\ &= \frac{9kT}{64\pi} q_{\perp} \left(q_{\parallel}^2 \frac{\xi_{\perp}^3}{\xi_{\parallel}} + \frac{2}{9} q_{\parallel}^2 \xi_{\parallel} \xi_{\perp}\right), \\ \delta K_2 &= \frac{3kT}{64\pi} \frac{q_{\parallel}}{(D_{\parallel}D_{\perp})^{1/2}} \frac{|C_{\perp}|^2}{\bar{a}} \left(1 + \frac{2D_{\parallel}}{9D_{\perp}}\right) \\ &= \frac{3kT}{64\pi} q_{\perp} \left(q_{\parallel}^2 \frac{\xi_{\perp}^3}{\xi_{\parallel}} + \frac{2}{9} q_{\parallel}^2 \xi_{\parallel} \xi_{\perp}\right), \\ \delta K_3 &= \frac{kT}{12\pi} q_{\parallel}^3 \left(\frac{D_{\parallel}}{D_{\perp}}\right)^{1/2} \frac{|C_{\perp}|}{\bar{a}} = \frac{kT}{24\pi} q_{\parallel}^2 q_{\perp} \xi_{\parallel} \xi_{\perp}.\end{aligned}\quad (3.8)$$

All three elastic constants diverge as ξ^2 in three dimensions. $\delta K_1/\delta K_2 = 3$ is not special to the third dimension. It holds in any dimension near the NC transition.

C. Lifshitz point

$$\begin{aligned}\delta K_1 &= \frac{kT}{4\pi} q_{\parallel}^2 \left(\frac{D_{\perp}}{2C_{\parallel}}\right)^{1/2} \ln \frac{\Lambda^2}{a} + \frac{kT}{32\pi} \left(\frac{2C_{\parallel}}{D_{\perp}}\right)^{1/2} \ln \frac{\Lambda^2}{a}, \\ \delta K_2 &= \frac{kT}{2\pi} q_{\parallel}^2 \left(\frac{D_{\perp}}{2C_{\parallel}}\right)^{1/2} \ln \frac{\Lambda^2}{a} + \frac{kT}{32\pi} \left(\frac{2C_{\parallel}}{D_{\perp}}\right)^{1/2} \ln \frac{\Lambda^2}{a}, \\ \delta K_3 &= \frac{kT}{12\pi} q_{\parallel}^2 \left(\frac{2C_{\parallel}}{a}\right)^{1/2} = \frac{kT}{12\pi} q_{\parallel}^2 \xi_{\parallel}.\end{aligned}\quad (3.9)$$

K_3 diverges as the correction length in the third direction, ξ_{\parallel} , while K_1 and K_2 are only slightly divergent.

ACKNOWLEDGMENTS

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APPENDIX A: IMPROVEMENTS ON THE MODEL

In order to modify Eq. (2.3) to allow an AC transition we include a nonlocal term

$$\frac{1}{2} \int d^3r b m^2(r) \vec{\nabla}_{\perp} m(r) \cdot \vec{\nabla}_{\perp} m(r)$$

in βH_4 with $b < 0$. The effect of this term is to drive the coefficient of k_{\perp}^2 negative as the smectic order parameter m grows in the smectic-A phase as the temperature decreases. It thus has the potential to induce an AC transition. In terms of the de Gennes order parameter $\psi = |\psi| e^{i\varphi}$ the resulting free energy is

$$\begin{aligned}F &= \frac{1}{2} \int d^3r \{a |\psi|^2 + C_{\parallel} |\nabla_{\parallel} \psi|^2 + C_{\perp} |\nabla_{\perp} \psi|^2 + D_{\perp} |\nabla_{\perp}^2 \psi|^2 \\ &\quad + 3u |\psi|^4 + b [|\psi|^2 (\nabla_{\perp} |\psi|)^2 + \frac{1}{2} |\psi|^2 |\nabla_{\perp} \psi|^2]\},\end{aligned}\quad (A1)$$

with $|\psi|$ constant and $\varphi = \vec{k}_{\perp} \cdot \vec{r}_{\perp}$. Equation (A1) is minimized when

$$|\psi|^2 (C_{\perp} + b |\psi|^2 + D_{\perp} k_{\perp}^2) k_{\perp}^2 = 0. \quad (A2)$$

Hence an A to C transition occurs when

$$C_{\perp} + b |\psi|^2 = 0, \quad (A3)$$

where

$$|\psi|^2 = (a'/6u)(T_{NA} - T)/T_{NA}. \quad (A4)$$

Equation (A3) is solved to give the phase boundary between the smectic-A phase and the smectic-C phase. For $b < 0$, we have

$$T_{AC} = T_{NA} [1 - (6u/a' |b|) C_{\perp}]. \quad (A5)$$

The resulting phase diagram is shown in Fig. 3(b).

APPENDIX B: DERIVATION OF WARD IDENTITIES

In this appendix we will derive Ward identities for the vertices coupling n_i to m which can be used to show that perturbation theory maintains rotational invariance. There are two vertices coupling n_i to m that are of interest:

$$\Gamma_i(\vec{x}_1, \vec{x}_2, \vec{x}_3) = \frac{1}{2} \frac{\delta G^{-1}(\vec{x}_1, \vec{x}_2)}{\delta n_i(\vec{x}_3)} \quad (B1)$$

$$\Gamma_{ij}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4) = \frac{1}{4} \frac{\delta G^{-1}(\vec{x}_1, \vec{x}_2)}{\delta n_i(\vec{x}_3) \delta n_j(\vec{x}_4)}. \quad (B2)$$

The vertex functions appearing in the text are related to the above via

$$\begin{aligned}\Gamma_i(\vec{k}, \vec{q}) &= \int d^3(x_1 - x_2) d^3x_3 e^{-i\vec{q} \cdot (\vec{x}_1 - \vec{x}_2)} \\ &\quad \times e^{-i\vec{k} \cdot \vec{x}_3} \Gamma_i(\vec{x}_1, \vec{x}_2, \vec{x}_3),\end{aligned}\quad (B3)$$

$$\begin{aligned}\Gamma_{ij}(\vec{k}_1, \vec{k}_2, \vec{q}) &= \int d^3(x_1 - x_2) d^3x_3 d^3x_4 \\ &\quad \times [e^{-i\vec{q} \cdot (\vec{x}_1 - \vec{x}_2)} e^{-i\vec{k}_1 \cdot \vec{x}_3} \\ &\quad \times e^{-i\vec{k}_2 \cdot \vec{x}_4} \Gamma_{ij}(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4)].\end{aligned}\quad (B4)$$

Combining Eqs. (B1)–(B4), we obtain

$$\lim_{\vec{k} \rightarrow 0} \Gamma_i(\vec{k}, \vec{q}) = \frac{1}{2} \frac{\partial G^{-1}(\vec{q})}{\partial n_i}, \quad (B5)$$

$$\lim_{k_1, k_2 \rightarrow 0} \Gamma_{ij}(\vec{k}_1, \vec{k}_2, \vec{q}) = \frac{1}{4} \frac{\partial^2 G^{-1}(\vec{q})}{\partial n_i \partial n_j}. \quad (B6)$$

But $G^{-1}(\vec{q})$ depends only on $q_{\parallel}^2 = (\vec{n} \cdot \vec{q})^2$ and $q_{\perp}^2 = q^2 - q_{\parallel}^2$. Therefore we have

$$\Gamma_i(0, \vec{q}) = \frac{1}{2} \left(q_i \frac{\partial G^{-1}}{\partial q_3} - q_3 \frac{\partial G^{-1}}{\partial q_i} \right) = q_i q_3 \left(\frac{\partial G^{-1}}{\partial q_3^2} - \frac{\partial G^{-1}}{\partial q_i^2} \right), \quad (\text{B7})$$

$$\Gamma_{ij}(0, 0, \vec{q}) = \frac{1}{2} \left(q_i \frac{\partial \Gamma_j}{\partial q_3} - q_3 \frac{\partial \Gamma_j}{\partial q_i} \right). \quad (\text{B8})$$

Equations (B7) and (B8) can be used to show that the contribution to π_{ij} from diagram 4(b) ($\pi_{ij}^{(2)}$) cancels the zero momentum contribution from diagram 4(a) ($\pi_{ij}^{(1)}$):

$$\begin{aligned} \pi_{ij}^{(2)} &= \int \Gamma_{ij}(0, 0, \vec{q}) G(\vec{q}), \quad i, j = 1, 2; \\ \pi_{ij}^{(2)} &= \frac{1}{2} \int \left(q_i \frac{\partial \Gamma_j}{\partial q_3} - q_3 \frac{\partial \Gamma_j}{\partial q_i} \right) G \\ &= -\frac{1}{2} \int \left(q_i \frac{\partial G}{\partial q_3} - q_3 \frac{\partial G}{\partial q_i} \right) \Gamma_j \\ &= \frac{1}{2} \int \left(q_i \frac{\partial G^{-1}}{\partial q_3} - q_3 \frac{\partial G^{-1}}{\partial q_i} \right) \Gamma_j G^2 \\ &= \int \Gamma_i(0, \vec{q}) \Gamma_j(0, \vec{q}) G^2(\vec{q}) = -\pi_{ij}^{(1)} \quad (\vec{q} = 0). \end{aligned} \quad (\text{B9})$$

This result is used in Eq. (3.6).

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