Unified Landau theory for the nematic, smectic A, and smectic C phases of liquid crystals*

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A unified Landau theory is introduced for the nematic, smectic A, and smectic C phases using the director $\vec{n}$ for the nematic order parameter, the complex order parameter ψ for the smectic planes, and the vector $\vec{\beta}$ for the smectic C dipolar order. The phase diagram is studied and a possible second-order triple point is predicted. The liquid structure factor near the nematic–smectic C phase transition is calculated and found to be in semiquantitative agreement with the x-ray experiments. All three Frank elastic constants are predicted to diverge near a second-order nematic–smectic C transition. The compressive instability near the smectic A–smectic C phase transition is explained in the present model.

I. INTRODUCTION

Landau theories for the nematic–smectic A phase transition[1,2] and for the smectic A–smectic C phase transition[3,4] have been studied recently. In this paper we introduce a unified Landau theory applicable to all three phases. This theory permits a study of the nematic–smectic C phase transition and of the triple point.

The original theory of liquid crystals was the Oseen-Frank[5,6] elastic theory of the nematic phase. It consisted of an expression for the free energy as a functional of the (unit vector) director $\vec{n}(\vec{r})$ [our Eq. (1)]. This theory was extended to a smectic A phase by deGennes[1] and by McMillan[2] who introduced a complex order parameter $\psi(\vec{r})$ to describe the smectic planes. The second-order smectic A–nematic phase transition is presently being studied intensively,[7-16] both theoretically and experimentally. deGennes[3] introduced a Landau theory for the smectic A–smectic C phase transition using a tilt angle between the director and the normal to the smectic planes as an order parameter. McMillan[4] proposed a microscopic theory of the smectic C phase based on the electric dipole-dipole interaction and derived a Landau theory for the smectic A–smectic C phase transition using the dipole orientational order parameter. This physical picture of the smectic C phase has been controversial and is not yet universally accepted. Meyer[17] has pointed out that one should use a linear combination of tilt and orientation as the order parameter in the smectic C phase and that deGennes's and McMillan's theories are limiting cases. Doane *et al.*[18] have observed the orientational freezeout in TBBA with an NMR technique. In addition there is increasing chemical evidence[19] that electric dipoles on the molecular end groups induce the smectic C phase. In the present paper we will adopt McMillan's physical picture of the smectic C phase and use the orientational order parameter $\vec{\beta}(\vec{r})$ to describe that phase.

deGennes[20] has already proposed a Landau theory to describe the nematic–smectic C transition using only the ψ and $\vec{n}$ order parameters; the tilt angle is already specified once ψ and $\vec{n}$ are known and no new order parameter for the smectic C phase is necessary. The preferred tilt direction is introduced (somewhat artificially) as an additional parameter (not an order parameter) and is then integrated over. The predictions of deGennes's theory are different from our theory and one can decide experimentally which is correct.

Our principle results are the following. The nematic–smectic C phase transition may be second order and one may have a triple point of second-order phase transitions. The computed liquid structure factor in the nematic phase near the nematic–smectic C transition is in semiquantitative agreement with the x-ray data[21]; the remaining deviations appear to be due to the neglect of director fluctuations. deGennes's nematic–smectic C theory is in conflict with the x-ray data. All three elastic constants are renormalized near the nematic–smectic C transition with the renormalization proportional to ξ, the correlation length. deGennes's theory predicts a renormalization proportional to $\xi^{3/2}$. The layer compression experiments[22] near the smectic A–smectic C transition can be explained with the present theory.

II. THE LANDAU THEORY

We now introduce the various terms in the free energy. We begin with the Oseen-Frank elastic theory of the nematic phase

$$F_1 = \int d^3r \{\tfrac{1}{2}K_{11}(\vec{\nabla}\cdot\vec{n})^2 + \tfrac{1}{2}K_{22}[\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2 + \tfrac{1}{2}K_{33}[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2 - \tfrac{1}{2}\chi_a(\vec{n}\cdot\vec{H})^2\}, \quad (1)$$

where $\vec{n}(\vec{r})$ is the unit vector director, $\vec{H}$ is the

magnetic field, χ_a is the anisotropic part of the susceptibility, and K_{ii} are the three elastic constants.

We next consider the complex smectic order parameter $\psi(\vec{r})$. The free energy is

$$F_2 = \int d^3r[a|\psi|^2 + \tfrac{1}{2}b|\psi|^4 + c_{\parallel}|(\vec{n}\cdot\vec{\nabla} - iq_0)\psi|^2 + c_{\perp}|\vec{n}\times(\vec{\nabla} - iq_0\vec{\beta})\psi|^2]. \quad (2)$$

With $\vec{\beta} = 0$ this is the expression used previously[1,2] in the smectic A Landau theory. The term proportional to $\vec{\beta}$ is the linear coupling between tilt angle and dipolar order parameter derived previously.[4]

The third part of the free energy involves the vector orientational order parameter $\vec{\beta}(\vec{r})$. According to Ref. 4 this order parameter is the average electric dipole moment per molecule, perpendicular to the long molecular axis, of the dipole on one end of the molecule. The dipole moment on the opposite end of the molecule points in the opposite direction so that the smectic C phase is not ferroelectric. With the molecules sitting on planes, the dipole moments on the same end of neighboring molecules are parallel (see Fig. 1). In the absence of smectic order the positions of the molecules are random and the dipole-dipole interaction averages to zero. When the molecules are organized into planes, the parallel dipole moments are closer than the antiparallel dipoles and there is a net interaction. This means that one cannot include terms proportional only to $\vec{\beta}^2$ in the free energy; terms involving $\vec{\beta}$ must be proportional to some power of $|\psi|^2$. Keeping the lowest-order terms in a series expansion, we write

$$F_3 = \int d^3r\{e|\vec{\beta}|^2 + \tfrac{1}{2}f|\vec{\beta}|^4 + \tfrac{1}{2}d_{11}(\vec{\nabla}\cdot\vec{\beta})^2 + \tfrac{1}{2}d_{22}[\vec{n}\cdot(\vec{\nabla}\times\vec{\beta})]^2 + \tfrac{1}{2}d_{33}[\vec{n}\times(\vec{\nabla}\times\vec{\beta})]^2\}|\psi|^2 . \quad (3)$$

From its definition $\vec{\beta}$ must be perpendicular to $\vec{n}$:

$$\vec{\beta}\cdot\vec{n} = 0. \quad (4)$$

The total free energy is the sum of these three terms:

$$F = F_1 + F_2 + F_3. \quad (5)$$

We assume the following temperature dependences

$$a = a_0(T - T_1), \quad (6)$$

$$e = e_0(T - T_2), \quad (7)$$

with the other parameters temperature independent.

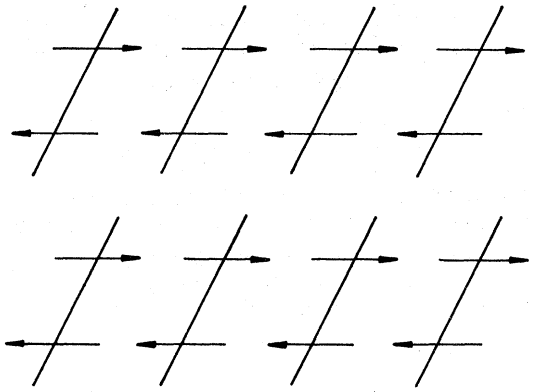

FIG. 1. Molecular order in the smectic C phase according to the microscopic theory[4] with molecular long axes aligned, the molecules sitting on planes, and the electric dipole moments (arrows) aligned.

III. PHASE DIAGRAM

We first study the phase diagram $b > 0$ so that the nematic–smectic A transition is second order. We work within the mean field approximation, neglecting fluctuations of the order parameters, and choose the order parameters to minimize the free energy. We choose

$$\psi = \psi_0 e^{iq_z z + iq_x x}, \quad (8)$$

$$\vec{\beta} = \beta_0\hat{x}, \quad (9)$$

$$\vec{n} = \hat{z}. \quad (10)$$

The free energy is minimal with

$$q_z = q_0, \quad q_x = q_0\beta_0, \quad (11)$$

and is given by

$$F = a\psi_0^2 + \tfrac{1}{2}b\psi_0^4 + e\beta_0^2\psi_0^2 + \tfrac{1}{2}f\beta_0^4\psi_0^2, \quad (12)$$

after integrating over a unit volume. Minimizing F with respect to ψ_0 and β_0, we find

$$(a + b\psi_0^2 + e\beta_0^2 + \tfrac{1}{2}f\beta_0^4)\psi_0 = 0, \quad (13)$$

$$(e + f\beta_0^2)\beta_0\psi_0^2 = 0. \quad (14)$$

We first take the case $T_1 > T_2$. Then for $T > T_1$ we find the nematic phase

$$\psi_0 = \beta_0 = 0, \quad T > T_1. \quad (15)$$

For $T_2 < T < T_1$ we find the smectic A phase

$$\psi_0^2 = a_0(T_1 - T)/b, \quad \beta_0 = 0, \quad T_2 < T < T_1; \quad (16)$$

and for $T < T_2$ we find the smectic C phase

$$\psi_0^2 = a_0(T_1 - T)/b + e_0^2(T_2 - T)^2/2bf, \quad \beta_0^2 = e_0(T_2 - T)/f, \quad T < T_2. \quad (17)$$

Both phase transitions are second order with the

relevant order parameter vanishing continuously at the phase transition. For the other case $T_2 > T_1$ we find the nematic phase at high temperature.

$$\psi_0 = 0, \quad T > T_{CN} \approx T_1 + e_0^2(T_1 - T_2)^2/2a_0 f. \tag{18}$$

The free energy is independent of β_0 in this approximation; we will show below that the orientational order parameter β_0 is defined in the smectic droplets and has the value $(-e/f)^{1/2}$. For $T < T_{CN}$ we have the smectic C phase with

$$\begin{aligned} \psi_0^2 &= a_0(T_1 - T)/b + e_0^2(T - T_2)^2/2bf, \\ \beta_0^2 &= e_0(T_2 - T)/f, \quad T < T_{CN}, \end{aligned} \tag{19}$$

and the nematic–smectic C phase transition is second order; the smectic C phase has a finite tilt at the phase transition. The phase diagram is shown in Fig. 2 with the triple point at $T_1 = T_2$.

IV. FLUCTUATION MODES

We now find the energy of the director fluctuation modes in the smectic C phase. We assume a monodomain of smectic C and look for fluctuations about the minimum in free energy. We assume uniform flat smectic planes and write

$$\psi = \psi_0 e^{iq_0 e^* + iq_0 \beta_0 x}, \tag{20}$$

$$\vec{\beta} = \beta_0 \hat{x} + \sum_q \delta\vec{\beta}_q e^{i\vec{q}\cdot\vec{r}}, \tag{21}$$

$$\vec{n} = \hat{z} + \sum_q \delta\vec{n}_q e^{i\vec{q}\cdot\vec{r}}, \tag{22}$$

with β_0 and ψ_0 given by Eq. (19). There are four

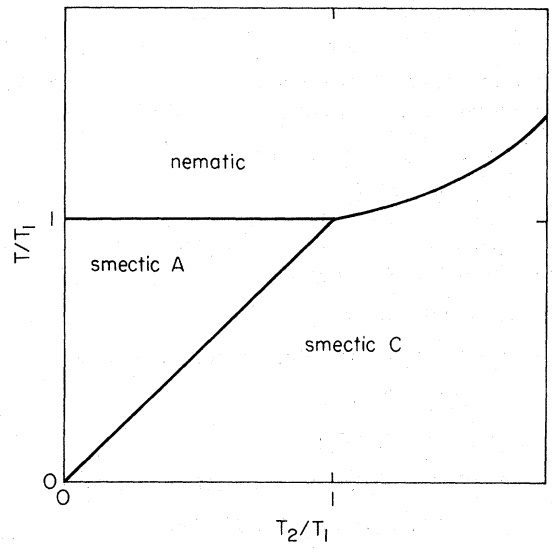

FIG. 2. Phase diagram for the nematic, smectic A, and smectic C phases; all three phase transitions are permitted to be second order.

modes, two each for $\delta\beta_q$ and δn_q polarized in the x and y directions. Only one mode is hydrodynamic (small energy at long wavelength); it is the linear combination $(\delta n_q - \delta\beta_q)/\sqrt{2}$ polarized in the y direction and has the energy

$$\tfrac{1}{4}(K_{11} + d_{11})q_y^2 + \tfrac{1}{4}(K_{22} + d_{22})q_x^2 + \tfrac{1}{4}(K_{33} + d_{33})q_z^2. \tag{23}$$

Recall that in the nematic phase there are two modes, one with energy

$$\tfrac{1}{2}\tilde{K}_{11}(q_x^2 + q_y^2) + \tfrac{1}{2}\tilde{K}_{33}q_z^2, \tag{24}$$

and a second with energy

$$\tfrac{1}{2}\tilde{K}_{22}(q_x^2 + q_y^2) + \tfrac{1}{2}\tilde{K}_{33}q_z^2. \tag{25}$$

The elastic constants in the nematic phase are renormalized by smectic order parameters fluctuations whereas the bare elastic constants K_{ii} appear in Eq. (23). Durand and co-workers[23] have observed this mode in the smectic C phase and find elastic constants comparable to those in nematics.

V. X-RAY SCATTERING

deVries[24] and Chistyakov[25] have observed diffuse scattering of x rays in the nematic phase of materials with a smectic C phase a lower temperature. deVries has correctly interpreted the scattering as Bragg scattering from tilted cybotactic groups or tilted smectic droplets in the nematic phase. This is a pretransition phenomenon characteristic of the nematic–smectic C phase transition; the droplets grow in size as one approaches the phase transition. McMillan[21] then made quantitative measurements of the liquid structure using x rays for p-n-heptyloxyazoxy-benzene (HAB). In this section we calculate the liquid structure factor using the Landau theory and compare with McMillan's measurements.

In the nematic phase the average value of the smectic order parameter is zero; however there are thermal fluctuations of ψ as small regions of the nematic fluctuate into the smectic C phase. We take these thermal fluctuations into account by writing

$$\psi(\vec{r}) = \sum_q \psi_q e^{i\vec{q}\cdot\vec{r}}. \tag{26}$$

The x-ray scattering intensity is proportional to the thermal average of $|\psi_q|^2$.[2] We assume that the orientational order parameter is constant over one smectic droplet, but we take a thermal average over its magnitude and direction.

$$\vec{\beta}(\vec{r}) = \hat{x}\beta_0 \cos\phi + \hat{y}\beta_0 \sin\phi \ . \tag{27}$$

Finally, we neglect thermal fluctuations of the director

$$\vec{n}(\vec{r}) = \hat{z}. \tag{28}$$

Keeping quadratic terms in ψ_q, the free energy is

$$F = \sum_q \epsilon_q |\psi_q|^2, \tag{29}$$

where

$$\epsilon_q = a + c_{\parallel}(q_z - q_0)^2 + c_{\perp}(\vec{q}_{\perp} - q_0\vec{\beta})^2 + (e + \tfrac{1}{2} f\beta_0^2)\beta_0^2 \tag{30}$$

and $\vec{q}_{\perp} = \vec{q} - \vec{n}(\vec{n}\cdot\vec{q})$. Averaging over thermal fluctuations of $\psi_{q'}$, we have

$$\langle |\psi_q|^2 \rangle \propto kT \int d^2\beta \frac{1}{\epsilon_q} \prod_{q'} \frac{1}{\epsilon_{q'}} \Big/ \int d^2\beta \prod_{q'} \frac{1}{\epsilon_{q'}}. \tag{31}$$

Taking a cutoff wave number of the order of q_0, we find

$$\prod_{q'} \frac{1}{\epsilon_{q'}} = \exp\Big(-\sum_{q'} \ln\epsilon_{q'}\Big) = \exp(\text{const} - q_0 A V a'/8\pi^2 c_{\perp}), \tag{32}$$

where

$$a' = a + e\beta_0^2 + \tfrac{1}{2} f\beta_0^4. \tag{33}$$

In (32), the sample volume V is included explicitly and A is a number of order unity which depends on the ratio of the transverse and longitudinal cutoff wave numbers. Equation (32) is correct for small $a'/c_{\parallel}q_0^2$; this function is the probability of finding an orientational order parameter β_0; this probability is maximum for

$$\beta_0^2 = -e/f \tag{34}$$

and we use this value in Eq. (20). Integrating over ϕ, we find

$$\langle |\psi_q|^2 \rangle = kT[a' + c_{\parallel}(q_z - q_0)^2 + c_{\perp}(q_{\perp} - q_0\beta_0)^2]^{-1/2} \times [a' + c_{\parallel}(q_z - q_0)^2 + c_{\perp}(q_{\perp} + q_0\beta_0)^2]^{-1/2}. \tag{35}$$

At the second-order phase transition ($a' = 0$) the liquid structure factor has an inverse square-root singularity at $q_z = q_0$, $q_{\perp} = \beta_0 q_0$. This singularity is rounded by three factors: (i) if one is not at the phase transition $a' \neq 0$; (ii) thermal fluctuations of β_0 smear out the liquid structure factor even at the phase transition; (iii) thermal fluctuations of the director with a wavelength of the order of a correlation length will rotate the smectic droplets in real space and further smear the structure factor. We have not yet been able to include either type of thermal fluctuations in the liquid structure factor calculation.

In Fig. 3 we show a fit of the theoretical structure factor to the x-ray data[21] as a function of $q_{\perp}$ for $q_z = q_0$. Only the parameter a' is varied as a function of temperature; the fitting parameters are given in Table I. One can obtain a somewhat better fit by decreasing β_0 with increasing temperature. The temperature dependence of a' is decidedly nonlinear; however, one should be cautious in taking the results of the fit seriously because the theory is not quantitative. The fit is at least semiquantitative and is the strongest evidence that the Landau theory is correct. The most probable tilt angle ($\theta = \tan^{-1}\beta_0$) at 96 °C (nematic phase) is 30° whereas at 94 °C (smectic C phase) the tilt angle is 38°.[21] Thus the tilt angle is quasi-

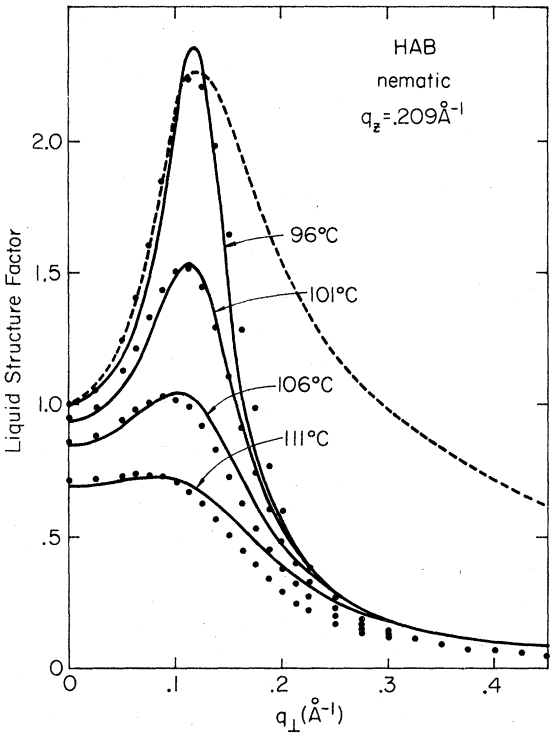

FIG. 3. Liquid structure of HAB at four temperatures versus $q_{\perp}$ for $q_z = q_0 = 0.209$ Å^{-1}. The points are from a smooth curve fitted to McMillan's x-ray data; the solid curves are the fit of our theory to the data points with parameters given in Table I; the dashed curve is the fit of deGennes's nematic–smectic C theory to the data points at 96 °C.

TABLE I. Values of the parameters from Eq. (34) used to fit the x-ray data in Fig. 3.

T (°C)	β_0	$a'/c_{\perp}q_0^2$
96	0.585	0.017
101	0.585	0.0405
106	0.585	0.09
111	0.585	0.185

continuous through this (first-order) phase transition.

The ratio of correlation lengths found by fitting the q_z dependence near the peak is

$$\xi_{\parallel}/\xi_{\perp}=(c_{\parallel}/c_{\perp})^{1/2}\approx 4.5. \tag{36}$$

From the value of a' in Table I the transverse correlation length at 96 °C is

$$\xi_{\perp}\equiv(c_{\perp}/a')^{1/2}\approx 37\ \text{Å}. \tag{37}$$

The fitting procedure which neglects smearing effects tends to overestimate a' and underestimate the correlation lengths. The correlation length of 67 Å quoted in the experimental paper[21] is a misinterpretation.

One feature of the experimental data is not fit by the theoretical model. According to the theory for large $|q_z-q_0|$ the liquid structure should be independent of $q_\perp$. Experimentally the liquid structure factor is not constant in this region but is smaller for small $q_\perp$. Thermal fluctuations of the director smear the structure factor by rotating it around the origin. This will not smear the region with small $q_\perp$ but will smear out the large $q_\perp$ region. This effect will qualitatively explain the remaining discrepancy between theory and experiment.

We can also compare deGennes's nematic–smectic C Landau theory[20] with the x-ray measurements. With

$$\psi(\vec{r})=\sum_q \psi_q e^{iq_z z+i\vec{q}_\perp\cdot\vec{r}}, \tag{38}$$

$$\vec{n}(\vec{r})=\hat{z}, \tag{39}$$

the expression for the x-ray structure factor is

$$\langle|\psi_q|^2\rangle=\int\frac{d\phi\,kT}{\alpha+(q_z-q_v)^2/2M_V+(\vec{u}\cdot\vec{q}_\perp-q_T)^2/2M_T}, \tag{40}$$

where $\vec{u}$ is a unit vector perpendicular to $\vec{n}$

$$\vec{u}=\hat{x}\cos\phi+\hat{y}\sin\phi \tag{41}$$

and the cross term with mass M_{VT} is unimportant and has been neglected. Although the physical basis of the two theories is different, the expressions (34) and (40) for the liquid structure factor are similar, the only difference being the deGennes's theory has infinite mass in the third direction (perpendicular to $\vec{n}$ and $\vec{u}$) whereas our theory has a finite mass. This difference is responsible for the different predictions for the liquid structure factor and for the elastic constants. In Fig. 3 we show the fit of deGennes's nematic–smectic C theory to the x-ray data on HAB at 96 °C. The fit is poor with the predicted structure factor falling off as $1/q_\perp$ for large $q_\perp$ whereas the experimental structure factor (and our theory) falls off as $1/q_\perp^2$. We conclude that the free-energy expression written down by deGennes is incorrect.

VI. PRETRANSITION RENORMALIZATION OF ELASTIC CONSTANTS

Using the smectic A–nematic Landau theory deGennes[1] predicted a pretransition increase of elastic constants in the nematic phase due to smectic order parameter fluctuations. The physical argument is that bending or twisting the smectic droplets changes the interplanar spacing and costs energy; a splay distortion of the droplet preserves interplanar spacing and costs no energy. The renormalized elastic constants near a nematic–smectic A phase transition are

$$\tilde{K}_{11}=K_{11}\quad\text{(splay)} \tag{42}$$

$$\tilde{K}_{22}=K_{22}+\frac{kTq_0^2}{24\pi}\left(\frac{c_\perp^{\,2}}{ac_{\parallel}}\right)^{1/2}\quad\text{(twist)} \tag{43}$$

$$\tilde{K}_{33}=K_{33}+\frac{kTq_0^2}{24\pi}\left(\frac{c_{\parallel}}{a}\right)^{1/2}\quad\text{(bend)}. \tag{44}$$

For a smectic C monocrystal there is one distortion which costs no energy at long wavelength as discussed in Sec. IV. However this mode is polarized perpendicular to the tilt direction and for a distorted nematic there will be smectic C droplets tilted in all directions some of which will be distorted in an energetically unfavorable manner. Thus all three elastic constants will be renormalized near a nematic–smectic C phase transition. In order to calculate the renormalized elastic constants we will assume a uniform distortion of the director and calculate the free energy of the smectic order parameter fluctuations in the presence of this distortion. This calculation is similar to the calculation of susceptibility of a superconductor by Schmid.[26] To compute $\tilde{K}_{11}$ we assume a uniform splay distortion

$$\vec{n}(\vec{r})=\hat{z}+\epsilon\,x\hat{x}, \tag{45}$$

where ϵ is small. Then

$$\vec{\beta}(\vec{r})=\hat{x}\beta_0\cos\phi+\hat{y}\beta_0\sin\phi-\hat{z}\,x\epsilon\cos\phi. \tag{46}$$

Writing

$$\psi(\vec{r})=\Phi(\vec{r})\exp[iq_0(z+x\beta_0\cos\phi+y\beta_0\sin\phi+\tfrac{1}{2}\epsilon x^2)], \tag{47}$$

the smectic free energy can be written in the following form

$$F=\int d^3r\,\Phi^*\left[a'-c_{\parallel}\left(\frac{\partial}{\partial z}-iq_0\beta_0\epsilon x\cos\phi\right)^2-c_\perp\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\right]\Phi+\int d^3r\,\tfrac{1}{2}K_{11}\epsilon^2. \tag{48}$$

We find the diagonal form of the free energy by finding the eigenfunctions and eigenvalues of the free-energy operator [the differential operator in square brackets in Eq. (48)]. The eigenvalue equation is

$$\left[a' - c_{\parallel}\left(\frac{\partial}{\partial z} - iq_0\beta_0\epsilon x\cos\phi\right)^2 - c_{\perp}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right]\Phi_{n,k_y,k_z} = E_{n,k_y,k_z}\Phi_{n,k_y,k_z}. \quad (49)$$

This problem is equivalent to finding the eigenfunction of an electron in a uniform magnetic field.[27] The eigenvalues are

$$E_{n,k_y,k_z} = (c_{\parallel}c_{\perp})^{1/2}q_0\beta_0\epsilon\cos\phi(2n+1) + c_{\perp}k_y^2. \quad (50)$$

The eigenfunctions are localized in the z direction about

$$z_0 = k_z/q_0\beta_0\epsilon\cos\phi. \quad (51)$$

Writing the order parameter as a linear combination of normalized eigenfunctions

$$\Phi(\vec{r}) = \sum_{n,k_y,k_z} C_{n,k_y,k_z}\Phi_{n,k_y,k_z}(\vec{r}). \quad (52)$$

We find for the free energy per unit volume

$$F = \sum_{n,k_y,k_z} |C_{n,k_y,k_z}|^2 E_{n,k_y,k_z} + \tfrac{1}{2}K_{11}\epsilon^2. \quad (53)$$

The partition function is found by integrating over the amplitudes of the smectic order parameter fluctuations.

$$Z = \prod_{n,k_y,k_z}\int d^2C_{n,k_y,k_z}e^{-F/kT} = \left(\prod_{n,k_y,k_z}\frac{\pi kT}{E_{n,k_y,k_z}}\right)e^{-K_{11}\epsilon^2/2kT}. \quad (54)$$

The renormalized free energy (after integrating out the smectic order-parameter fluctuations) is

$$\tilde{F} = -kT\ln Z = \tfrac{1}{2}K_{11}\epsilon^2 - kT\sum_{n,k_y,k_z}\ln\left(\frac{\pi kT}{E_{n,k_y,k_z}}\right). \quad (55)$$

Since the energy is independent of k_z, the sum over k_z is easy; we sum over those values of k_z for which the center of the eigenfunction is inside the integration volume. Then

$$\sum_{k_z} = \frac{q_0\beta_0\epsilon\cos\phi}{2\pi}. \quad (56)$$

Some care is required in replacing $\sum_n$ by an integral; for any function $f(n)$

$$\int_0^{n_0} f(n)dn \approx \sum_{n=0}^{n_0-1} f(n+\tfrac{1}{2}) + \frac{1}{24}\left(\frac{df}{dn}\bigg|_{n_0} - \frac{df}{dn}\bigg|_0\right). \quad (57)$$

Using (57) we find the free energy per unit volume

$$\tilde{F} = \text{const} + \frac{1}{2}\left(K_{11} + \frac{kTq_0^2\beta_0^2\cos^2\phi(c_{\parallel}/a')^{1/2}}{24\pi}\right)\epsilon^2. \quad (58)$$

If we had simply replaced $\sum_n$ by $\int dn$ in Eq. (55), we would have obtained only the constant term in $\tilde{F}$. The entire correction to the elastic constant arises from the discrete nature of the eigenvalue spectrum. The use of Eq. (57) is only valid provided

$$(c_{\perp}c_{\parallel})^{1/2}q_0\beta_0\epsilon\cos\phi \ll a', \quad (59)$$

which limits the amplitude of distortion which one can use to measure the renormalized elastic constant. From (58) we define a renormalized (observable) splay elastic constant (after averaging over ϕ)

$$\tilde{K}_{11} = K_{11} + \frac{kTq_0^2}{24\pi}\left(\frac{c_{\parallel}}{a'}\right)^{1/2}\frac{\beta_0^2}{2} \quad \text{(splay)}. \quad (60)$$

A similar calculation for twist and bend distortions yields

$$\tilde{K}_{22} = K_{22} + \frac{kTq_0^2}{24\pi}\left(\frac{c_{\parallel}}{a'}\right)^{1/2}\left(\frac{c_{\perp}}{c_{\parallel}} + \frac{\beta_0^2}{2}\right) \quad \text{(twist)}, \quad (61)$$

$$\tilde{K}_{33} = K_{33} + \frac{kTq_0^2}{24\pi}\left(\frac{c_{\parallel}}{a'}\right)^{1/2} \quad \text{(bend)}. \quad (62)$$

These results reduce to the smectic A results when $\beta_0 = 0$. For HAB $\frac{1}{2}\beta_0^2 \approx 0.17$ and $c_{\perp}/c_{\parallel} = 0.05$. The renormalization of all three elastic constants is proportional to $\xi_{\parallel} = (c_{\parallel}/a')^{1/2}$ in our theory and to $\xi_{\parallel}^{3/2}$ in deGennes's theory. The elastic constant renormalization has been observed by Gruler[28] for homologs of HAB.

VII. COMPRESSIVE INSTABILITY

Ribotta, Meyer, and Durand[22] have observed a compression induced smectic A–smectic C phase change in a smectic A liquid crystal near the thermodynamic smectic A–smectic C transition. In the smectic C phase the molecules are tilted with respect to the plane normal and the spacing of the smectic planes is reduced. An externally applied stress compressing the layers can be relieved by tilting the molecules thus driving the liquid crystal into the smectic C phase. Ribotta *et al.* observed a threshold strain for tilting which is proportional to $T - T_2$. This behavior was explained using deGennes's Landau theory of the smectic A–smectic C phase transition which uses the tilt angle as the order parameter. In this section we show that the tilt threshold can also be explained using our unified Landau theory.

We begin with the liquid crystal in the smectic A phase with interplanar spacing $d = 2\pi/q_0$. The

liquid crystal is compressed suddenly so that the interplanar spacing is $d - \Delta d$. We now choose the order parameters so that the liquid crystal may be in either the smectic A or smectic C phase.

$$\psi(\vec{r}) = \psi_0 e^{iq_z z + iq_\perp x}, \tag{63}$$

$$\vec{n}(\vec{r}) = \hat{z}, \tag{64}$$

$$\vec{\beta}(\vec{r}) = \beta_0 \hat{x}. \tag{65}$$

We choose a coordinate system which tilts with the director. The interplanar spacing is held fixed

$$d - \Delta d = \frac{2\pi}{(q_z^2 + q_\perp^2)^{1/2}} = \frac{2\pi}{q_0 + \Delta q}, \tag{66}$$

where

$$\Delta q / q_0 = \Delta d / d. \tag{67}$$

We fix ψ_0 at its smectic A value

$$\psi_0^2 = -a/b. \tag{68}$$

The relevant terms in the free energy are

$$F/\psi_0^2 = c_\parallel [\Delta q - \tfrac{1}{2}(q_\perp^2/q_0)]^2 + c_\perp (q_\perp - q_0\beta_0)^2 + e\beta_0^2, \tag{69}$$

where the undetermined parameters are $q_\perp$ and β_0. We find these two parameters by minimizing the free energy with respect to each of them and find

$$\theta \approx \frac{q_\perp}{q_0} = 0, \quad \Delta q < q_0 \frac{c_\perp}{c_\parallel} \frac{e}{e + c_\perp q_0^2}, \tag{70}$$

$$\theta^2 \approx \frac{q_\perp^2}{q_0^2} = 2\frac{\Delta q}{q_0} - 2\frac{c_\perp}{c_\parallel}\frac{e}{e + c_\perp q_0^2}, \text{ otherwise} \tag{71}$$

which predicts a threshold compression with tilt angle squared proportional to compression above threshold. For a material with a smectic A–smectic C phase transition the threshold compression is proportional to $T - T_2$; for a material with no tendency to form a smectic C phase ($e = \infty$) the fractional compression at threshold is $c_\perp/c_\parallel \approx 0.05$.

Thus the predictions of our unified Landau theory agree with the predictions of deGennes's smectic A–smectic C Landau theory and with experiment.

VIII. CONCLUSIONS

We have written down a unified Landau theory for the nematic, smectic A, and smectic C phases which is an extension and synthesis of several previous theories. This theory reduces to the very successful nematic–smectic A Landau theory in the appropriate limit and describes the phase transition and compressive instability at the smectic A–smectic C transition. The theory predicts the possibility of a second-order nematic–smectic C phase transition and a second-order triple point. We have computed the elastic constant for the director fluctuation mode in the smectic C phase. We have also calculated the liquid structure factor and the renormalized elastic constants in the nematic phase near the nematic–smectic C phase transition. The calculated liquid structure factor is in semiquantitative agreement with the x-ray measurements. We have shown that deGennes's Landau theory of the nematic–smectic C phase transition is in conflict with the x-ray measurements.

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[1]P. G. deGennes, Solid State Commun. 10, 753 (1972).
[2]W. L. McMillan, Phys. Rev. A 6, 936 (1972).
[3]P. G. deGennes, C. R. Acad. Sci. B 274, 758 (1972).
[4]W. L. McMillan, Phys. Rev. A 8, 1921 (1973).
[5]C. W. Oseen, Trans. Faraday Soc. 29, 883 (1933).
[6]F. C. Frank, Disc. Faraday Soc. 25, 1 (1958).
[7]F. Brochard, J. Phys. (Paris) 34, 28 (1973); F. Janig and F. Brochard, J. Phys. (Paris) 35, 301 (1974).
[8]W. L. McMillan, Phys. Rev. A 9, 1720 (1974).
[9]B. I. Halperin, T. C. Lubensky, and S.-K. Ma, Phys. Rev. Lett. 32, 292 (1974).
[10]L. Cheung, R. B. Meyer, and H. Gruler, Phys. Rev. Lett. 31, 349 (1973).
[11]P. E. Cladis, Phys. Rev. Lett. 31, 1200 (1973).
[12]C.-C. Huang, R. S. Pindak, P. J. Flanders, and J. T. Ho, Phys. Rev. Lett. 33, 400 (1974).
[13]D. Salin, I. W. Smith, and G. Durand, J. Phys. (Paris) 35, L-165 (1974).
[14]K. C. Chu and W. L. McMillan, Phys. Rev. A 11, 1059 (1975).
[15]S. Torza and P. E. Cladis, Phys. Rev. Lett. 32, 1406 (1974).
[16]D. Djurek, J. Baturic-Rubcic, and K. Franulovic, Fifth International Liquid Crystal Conference (unpublished).
[17]R. B. Meyer, Fifth International Liquid Crystal Conference (unpublished).
[18]R. S. Parker, J. W. Doane, and D. L. Fishel, Fifth International Liquid Crystal Conference (unpublished).
[19]W. M. deJeu (private communication).
[20]P. G. deGennes, Mol. Cryst. Liq. Cryst. 21, 49 (1973).
[21]W. L. McMillan, Phys. Rev. A 8, 328 (1973).
[22]R. Ribotta, R. B. Meyer, and G. Durand, J. Phys. (Paris) 35, L-161 (1974).
[23]Y. Galerne, J. L. Martinand, G. Durand, and M. Veyssie, Phys. Rev. Lett. 29, 562 (1972).
[24]A. DeVries, Acta. Cryst. A 25, S135 (1969); Mol. Cryst. Liq. Cryst. 10, 31 (1970); 10, 219 (1970).
[25]I. G. Chistyakov and W. M. Chaikowsky, Mol. Cryst. Liq. Cryst. 7, 269 (1969).
[26]A. Schmid, Phys. Rev. 180, 527 (1969).
[27]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., London, 1964).
[28]H. Gruler, Z. Naturforsch. A 28, 474 (1973).