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Landau theory of the helicoidal C^* phase in smectic liquid crystals: Re-entrance of the smectic-C^* phase and order of the smectic-C–smectic-C^* transition

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We present a Landau theory for smectic liquid crystals in a magnetic field, and apply it to systems exhibiting the smectic-A (Sm-A), smectic-C (Sm-C), and smectic-C^* (Sm-C^*) phases; our theory provides a unified explanation of two phenomena, the temperature dependence of the pitch in the Sm-C^* phase and the re-entrance of the Sm-C^* phase. We find that the Sm-C^* phase is always re-entrant. Two types of phase diagrams are found, depending on the relative signs of two of the Landau parameters; in one case, the Sm-C^* phase is re-entrant only for fields greater than some value, while in the other case it is re-entrant for all field values (but the helicity has different sign above and below the Sm-C phase). The results are in qualitative agreement with experiment. The order parameter in the Sm-C^* phase has a well-developed domain structure only near the Sm-C–Sm-C^* boundary; a new feature is that the order parameter is almost sinusoidal at low temperatures, well below the boundary. We provide a complete analytical treatment of the Sm-C–Sm-C^* transition, extending previous results in the theory of commensurate-incommensurate transitions.

I. INTRODUCTION

Liquid crystals exhibiting the helicoidal smectic-C^* (Sm-C^*) phase are of considerable interest because of both their potential applications and their remarkable properties.[1] One such property is that the Sm-C^* phase is re-entrant in the presence of a magnetic field, Muševič *et al.*[2] observed (in the compound DOBAMBC) that there exists a range of magnetic fields for which the following sequence of phase transitions between the smectic A (Sm-A), smectic-C^*, and smectic-C (Sm-C) phases occurs with decreasing temperature T: Sm-$A \rightarrow$Sm-$C^* \rightarrow$Sm-$C \rightarrow$Sm-C^*. Another is that these compounds display a Lifshitz point where the wave number of the Sm-C^* phase goes to zero at the meeting point of the three phase boundaries Sm-A–Sm-C^*, Sm-A–Sm-C, and Sm-C–Sm-C^*; this point was predicted theoretically by Michelson[3] and has recently been observed by Seppen *et al.*[4]

For a Landau-theory discussion of the Sm-A, Sm-C, and Sm-C^* phases, a convenient order parameter (with two components n_x and n_y) is obtained by projecting the director $\hat{n}$ (a unit vector in the direction of the molecules) onto the x-y plane (which is parallel to the layers). In the Sm-A phase, the director is in the z direction (normal to the layers) and both components of the order parameter vanish ($n_x = n_y = 0$). In the Sm-C phase, the director is tiled at an angle θ to the z axis, the same angle in each layer, and both components of the order parameter are independent of z. In the Sm-C^* phase, the director rotates in a helical fashion in the z direction; the pitch of the helix is not a rational multiple of the thickness of the layers. The connection with commensurate-incommensurate systems is obvious; the Sm-A, Sm-C, and Sm-C^* phases correspond respectively to the disordered, commensurate and incommensurate phases. The driving term for the appearance of the helicoidal Sm-C^* phase is a Lifshitz invariant[5] in the Landau expression for the free-energy density.

Re-entrant transitions have been observed in other systems (the nematic–smectic-A transition and the superconducting-magnetic transition are familiar examples), but to the best of our knowledge the Sm-C^* phase is the first re-entrant incommensurate phase to be observed.

Several groups[6] have recently constructed a free-energy functional including the tilt angle θ and the polarization P in the absence of magnetic field. Good results were obtained, but the re-entrant phenomenon was not investigated.

This paper presents a theory (both numerical and analytical) of the Sm-C–Sm-C^* phase transition. Our approach differs from all previous work in this field in a major way—we do not make the one-harmonic approximation, but rather solve numerically the Euler-Lagrange equations for the order parameter; as we have shown previously,[7] the one-harmonic approximation is quite inadequate for these systems (for nonzero magnetic field), for it cannot describe a well-developed domain structure.

Section II gives a brief discussion of our free-energy functional. Section III uses this expression to treat the field-free case; in agreement with experiment, the wave number q of the Sm-C^* phase is predicted to depend quadratically on the tilt angle θ, either increasing or decreasing depending on the relative signs of two of the Landau coefficients. An extreme example (also explained by our theory) of this dependence occurs in PACMB where, with decreasing temperature, the helix unwinds and then winds in the opposite sense. Section IV provides a brief description of our numerical method, and Sec. V presents the phase diagrams found; some of these results have been reported previously.[7] The tricritical point found on the Sm-C–Sm-C^* line is explained in Sec. VI which analyzes the interaction of discommensurations, and shows that the first-order nature of the transition near the Lifshitz point is due to an attractive interaction between discommensurations. Some of the new results of Sec. VI are important for the theory of incommensurate-commensurate transitions. Section VII presents conclusions.

II. FREE ENERGY AND DIFFERENTIAL EQUATIONS

Our starting point is the following expression for the free energy relative to the Sm-A phase:

$$F=\int_{-\infty}^{\infty}\mathcal{F}(z)dz \ , \tag{1}$$

where the z direction is normal to the layers, and the free-energy density $\mathcal{F}$ is

$$\begin{aligned}\mathcal{F}=&\ A(n_x^2+n_y^2)+B_1(n_x^2+n_y^2)^2+C_1(n_x^2+n_y^2)^3\\&+D_1\left[\frac{dn_x}{dz}\right]^2+D_1\left[\frac{dn_y}{dz}\right]^2-D_2\left[n_x\frac{dn_y}{dz}-n_y\frac{dn_x}{dz}\right]\\&-D_3\left[n_x^3\frac{dn_y}{dz}-n_y^3\frac{dn_x}{dz}\right]-\tfrac{1}{2}\chi H^2 n_x^2 \ .\end{aligned} \tag{2}$$

The magnetic field H (which is in the x direction, parallel to the layer planes) couples only to the director, and so it is not necessary to include the polarization; more precisely, minimizing the free energy with respect to the polarization renormalizes the Landau coefficients, as discussed by other authors.[6] As usual in this kind of theory, only the Landau coefficient A is temperature dependent. We adopt the convention that the coefficient D_2 is positive (or zero); this amounts to the definition of the positive z direction. On the other hand, the Landau coefficient D_3 can be of either sign, so that if $D_2D_3<0$ the two terms compete, the one favoring a right-handed helicoidal structure, and the other a left-handed one; we show below that very different results are obtained according to the sign of D_3 relative to D_2. Unfortunately, the microscopic theory of liquid crystals is not sufficiently advanced to provide numerical values of the Landau coefficients, and we are forced to treat them as phenomenological parameters to be fitted to experiment.

Unlike previous theories, ours retains the proper symmetry; the free energy is expanded in powers of n_x and n_y rather than in powers of θ.

The D_3 term in Eq. (2) is all-important for our purposes (it is essential to explain the re-entrant Sm-C–Sm-C^* transition), but is not new with us. Žekš[6] has already introduced an analogous term in order to explain the temperature dependence of the helix pitch; more precisely, Žekš introduced a term differing by a factor and a perfect derivative from ours. Inclusion of the D_3 term enables one to explain both the temperature dependence of the wave number and the re-entrant Sm-C^* phase, and the two phenomena appear therefore to be closely related.

Equation (2) omits a fourth-order term $(B_2n_x^2n_y^2)$, allowed by symmetry, which has interesting consequences for the spatial dependence of the order parameter.[8] The expression also omits many sixth-order terms; the only such term (that involving the Landau parameter C_1) kept is necessary for stability when $D_3\neq 0$. The C_1 term is necessary in any case.[6]

Some restrictions on the Landau parameters: Obviously, $C_1\geq 0$ and $D_1\geq 0$ for stability. We assume that χ, the difference in the parallel and perpendicular susceptibilities, is greater than 0; the case $\chi<0$ is easily handled, and the phase diagram is merely sheared from that for $\chi>0$. We assume further that (i) $B_1>0$, (ii) $B_1>3D_2D_3/(8D_1)$, and (iii) $C_1>9D_3^2/(64D_1)$. The first of these makes the Sm-A–Sm-C transition second order; the second makes the Sm-A–Sm-C^* transition second-order in the absence of the field, but it may not be sufficient in its presence; the third is necessary for stability, but may not be sufficient.

With these restrictions, the Lifshitz point is at $H=H_{\mathrm{LP}}$, $A=A_{\mathrm{LP}}$, where $\frac{1}{2}\chi H_{\mathrm{LP}}^2=A_{\mathrm{LP}}=D_2^2/D_1$; the Sm-$A$–Sm-$C^*$ transition, if second order, occurs on the line

$$A=\frac{D_1}{4D_2^2}\left[\frac{D_2^2}{D_1}+\tfrac{1}{2}\chi H^2\right]^2 ,$$

with $H<H_{\mathrm{LP}}$; the Sm-A–Sm-C transition occurs along the line $A=\frac{1}{2}\chi H^2$, $H>H_{\mathrm{LP}}$. Determination of the Sm-C–Sm-C^* line requires numerical work.

The free energy as a function of T and H is found as follows: from Eqs. (1) and (2), the Euler-Lagrange equations are obtained as

$$\begin{aligned}&-D_1\frac{d^2n_x}{dz^2}-[D_2+\tfrac{3}{2}D_3(n_x^2+n_y^2)]\frac{dn_y}{dz}+(A-\tfrac{1}{2}\chi H^2)n_x\\&\qquad+2B_1n_x(n_x^2+n_y^2)+3C_1n_x(n_x^2+n_y^2)^2=0 \ ,\\&-D_1\frac{d^2n_y}{dz^2}+[D_2+\tfrac{3}{2}D_3(n_x^2+n_y^2)]\frac{dn_x}{dz}+An_y\\&\qquad+2B_1n_y(n_x^2+n_y^2)+3C_1n_y(n_x^2+n_y^2)^2=0 \ ;\end{aligned} \tag{3}$$

these are solved for n_x and n_y, and the solutions are then substituted into Eqs. (1) and (2).

The Euler-Lagrange equations must be solved numerically in the general case; an exception is the case of zero field, treated in Sec. III, for which an analytical solution is possible at all temperatures. With regard to approximate solutions of these equations, in a previous article[7] we investigated the one-harmonic and constant-amplitude approximations and found both to be unreliable except in limited regions of the phase diagram.

III. SMECTIC-C^* PHASE WITHOUT MAGNETIC FIELD

In the absence of a magnetic field, the solutions of the Euler-Lagrange equations (3) for the Sm-C^* phase are

$$n_x=n\cos(qz),\quad n_y=n\sin(qz)\ , \tag{4}$$

where the amplitude n and the wave number q are given by

$$3\left[C_1-\frac{9D_3^2}{64D_1}\right]n^4+2\left[B_1-\frac{3D_2D_3}{8D_1}\right]n^2+\left[A-\frac{D_2^2}{4D_1}\right]=0\ , \tag{5}$$

$$q=\frac{D_2}{2D_1}\left[1+\frac{3D_3n^2}{4D_2}\right]\ . \tag{6}$$

A factor D_2 is omitted in Eq. (3) of Ref. 7.

One sees easily that the Sm-A–Sm-C^* transition temperature T_c is given by $A=D_2^2/(4D_1)$; the Sm-A phase (with $n_x=n_y=0$) is stable if $T>T_c$, while the Sm-C^* phase is stable if $T<T_c$.

Note that our treatment neglects the term $B_2n_x^2n_y^2$ which is allowed by symmetry. If B_2 is nonzero, then the forms of Eq. (4) are no longer solutions of the Euler-Lagrange equations. Also, with $B_2=0$ and in the absence of the magnetic field, the Sm-C phase (which makes a brief appearance if $D_2D_3<0$) is infinitely degenerate with respect to the azimuthal angle; the degeneracy is reduced to twofold when the term involving B_2 is included.

It was already well verified by Žekš[6] that near T_c, when $n\sim\sin\theta\sim\theta$, the variation of n with T is consistent with Eq. (5). From Eq. (6) (which was also obtained by Žekš[6]) we see that q is linearly dependent on n^2. Figure 1 compares this prediction with the experimental results of Martinot-Lagarde *et al.*,[9] who performed measurements of θ and q on the same samples; the agreement is very good for all three compounds, including one with a divergent pitch at several degrees below T_c. More recent data (for DOBAMBC) on the temperature dependence of the pitch and the tilt angle are given in Ref. 10 but are not plotted in Fig. 1.

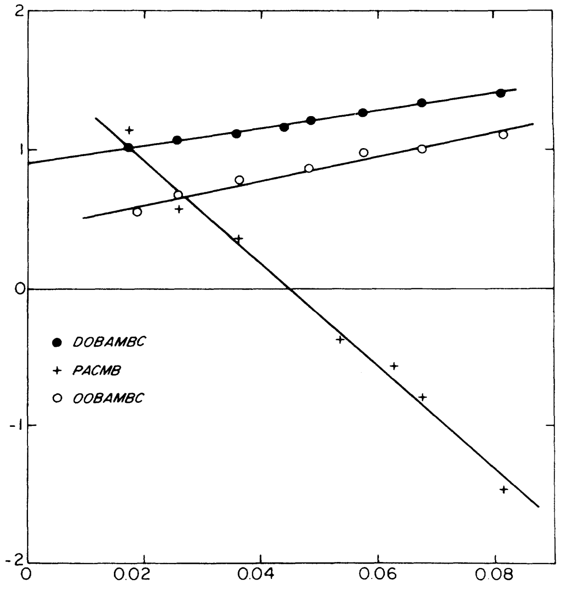

FIG. 1. The wave number q (in units of μm^{-1}) of the smectic-C^* phase in zero magnetic field as a function of θ^2 (θ is the tilt angle, in rad) for the compounds DOBAMBC, PACMB, and OOBAMBC. The data points are from Ref. 9; the lines are fits.

For DOBAMBC and OOBAMBC, the D_3 coefficient (deduced from Fig. 1) is positive, whereas for PACMB D_3 is negative. We show below that the topology of the H-T phase diagram is very different for these two cases ($D_3>0$ and $D_3<0$). Recall our convention $D_2>0$; we assume that the pitch has the same sign for small θ (i.e., the same sense of rotation of the helix) for the three compounds. More generally, if D_2 and D_3 have opposite signs then the pitch diverges at some temperature (which may not be physically accessible).

The properties of liquid crystals at the point on the temperature axis ($H=0$) for which $q\to0$ (and the pitch diverges) have scarcely been discussed in the literature, and so we provide the following. At the point $q=0$ or $n^2=-4D_2/3D_3$, the free energy of the Sm-C^* phase equals the free energy of the Sm-C phase. Thus we expect the fluctuations of q to be important. However, we do not find that there are also fluctuations of θ. Thus the specific heat will not exhibit any anomaly at this point (even on going beyond the mean-field theory). Since the tilt in these compounds is directly related to the spontaneous polarization of the smectic layers, we expect a divergence of the dielectric constant (in the case of an electric field parallel to the smectic layers) at this point. This can be understood since, when $q=0$, it costs no energy to rotate the tilted molecules.

Our results do not explain the maximum of the pitch p (proportional to $1/q$) observed in some compounds such as DOBAMBC, and therefore the free-energy functional of Eq. (2) may not be applicable for $|T-T_c|\lesssim0.5$ K.

IV. NUMERICAL SOLUTIONS FOR THE SMECTIC-C^* PHASE IN PRESENCE OF MAGNETIC FIELD

Reference 7 gives numerical results, and also investigates two approximations in order to provide a qualitative understanding of the results; these are the one-harmonic approximation (valid near the Sm-A–Sm-C^* transition temperature), and the constant-amplitude approximation (valid for large and negative values of A, that is, $A\lesssim-100$ for our parameter values). In the intermediate range of temperatures, neither approximation is adequate, and one must resort to numerical work.

The Euler-Lagrange equations [Eqs. (3)] were solved numerically as follows. Starting from approximate solutions (found variationally, or from the constant-amplitude or one-harmonic approximations, or from solutions at nearby points in parameter space), we linearized the equations for the deviations from the trial solutions, and used fourth-order finite-difference approximations for the derivatives to obtain a set of linear algebraic equations; these latter equations (of band form) were solved by elimination and back substitution. The results gave a new set of approximate solutions, and the procedure was iterated to convergence.

Useful checks on the accuracy of the solutions are provided by the first integral

$$-D_1\left[\left[\frac{dn_x}{dz}\right]^2+\left[\frac{dn_y}{dz}\right]^2\right]-\tfrac{1}{2}\chi H^2 n_x^2 + A(n_x^2+n_y^2) + B_1(n_x^2+n_y^2)^2 + C_1(n_x^2+n_y^2)^3 = \text{const}\ , \qquad (7)$$

and by the following relations:

$$2D_1\left\langle\left[\frac{dn_x}{dz}\right]^2+\left[\frac{dn_y}{dz}\right]^2\right\rangle = \left\langle D_2\left[n_x\frac{dn_y}{dz}-n_y\frac{dn_x}{dz}\right]+D_3\left[n_x^3\frac{dn_y}{dz}-n_y^3\frac{dn_x}{dz}\right]\right\rangle ,$$

$$\left\langle A(n_x^2+n_y^2)-\tfrac{1}{2}\chi H^2 n_x^2 + D_1\left[\left[\frac{dn_x}{dz}\right]^2+\left[\frac{dn_y}{dz}\right]^2\right] - D_2\left[n_x\frac{dn_y}{dz}-n_y\frac{dn_x}{dz}\right]+2B_1(n_x^2+n_y^2)^2 - 2D_3\left[n_x^3\frac{dn_y}{dz}-n_y^3\frac{dn_x}{dz}\right]+3C_1(n_x^2+n_y^2)^3\right\rangle = 0\ , \qquad (8)$$

where the angular brackets denote spatial averages; Eqs. (8) follow from the requirement that, at its minimum, the free energy must be a minimum with respect to the transformations $(n_x,n_y)\rightarrow(\lambda n_x,\lambda n_y)$ and $z\rightarrow\mu z$. Equations (7) and (8) were satisfied to one part in 10^8, even in the most extreme cases.

V. PHASE DIAGRAM

Our expression for the free energy contains too many parameters for a full investigation of the phase diagram, and so we have chosen what we believe to be representative values; more limited calculations for other sets of parameters show the same qualitative behavior. The numerical calculations were done for the choices $B_1=50$, $C_1=500$, $D_1=1$, $D_2=2$, and D_3 variable. The units of the order parameter, the length and the free energy can be scaled so that our results are actually more generally valid (although of course the amplitude of the order parameter must remain less than 1). Unfortunately, inconsistencies in published data prevent a quantitative comparison with experiment.

In Figs. 2 and 3 we show calculated phase diagrams with A as the ordinate, $\sqrt{\chi}H$ as the abscissa, and D_3 as the parameter. The Lifshitz point is located at the meeting of the three lines Sm-A–Sm-C^*, Sm-A–Sm-C, and Sm-C–Sm-C^*, specifically at $\chi H^2=8, A=4$ for the above set of parameters. The following is a summary of the results.

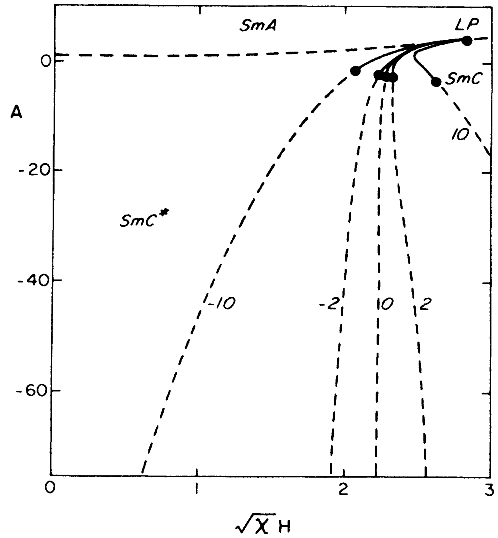

FIG. 2. Phase diagram in the A-H plane showing the regions of stability of the smectic-A (Sm-A), smectic-C (Sm-C), and smectic-C^* (Sm-C^*) phases (for the choices $B_1=50$, $C_1=500$, $D_1=1$, $D_2=2$ for the Landau parameters); the Landau parameter D_3 has the values 10, 2, 0, -2, and -10. First- and second-order transitions are denoted by solid and dashed lines, respectively. The three transition lines meet at the Lifshitz point (LP). The Sm-C–Sm-C^* transition is first order near the Lifshitz point, but second order farther away; the changeover occurs at the tricritical point (dot).

(1) If $D_3=0$, the Sm-C^* phase is not re-entrant; for A negative enough, the Sm-C–Sm-C^* line is parallel to the A axis.

(2) The case $D_3=0$ is very special, however, for if D_3 is different from zero, then the Sm-C^* phase is re-entrant whether $D_3>0$ or $D_3<0$; but very different behavior for

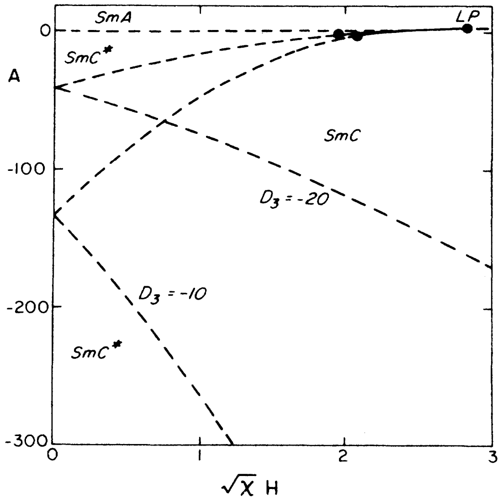

FIG. 3. Phase diagram in the A-H plane for $D_3=-10$ and -20; the values of the other Landau parameters are given in the caption to Fig. 2. The Sm-C^* phases have different signs of the helicity above and below the Sm-C phase.

the Sm-C–Sm-C^* line is obtained, depending on the sign of D_3 (relative to D_2).

(3) If $D_2 D_3 > 0$, the re-entrant sequence Sm-$A \rightarrow$Sm-$C^* \rightarrow$Sm-$C \rightarrow$Sm-C^* occurs with decreasing temperature, but only if the magnetic field H is larger than some value (which depends on D_3).

(4) If $D_2 D_3 < 0$, the Sm-C^* phase is re-entrant for all values of the magnetic field H. Figure 3 shows examples. In this case ($D_2 D_3 < 0$), the Sm-C–Sm-C^* line is in fact divided into two lines. The upper line begins at the Lifshitz point and goes down; it meets the lower line on the A axis at the point where the wave number q vanishes (and the pitch diverges). If D_3 is not too low (it is the case for $D_3 = -2$ in Fig. 2), this point is located at very large negative values of A and may not be physically accessible.

(5) There is another important difference between the cases $D_2 D_3 > 0$ and $D_2 D_3 < 0$. If $D_2 D_3 > 0$, the two Sm-C^* phases appearing in the sequence Sm-A–Sm-C^*–Sm-C–Sm-C^* have the same sense of rotation for the helix, whereas if $D_2 D_3 < 0$, the sense of rotation is different for the two Sm-C^* phases. We emphasize that the two Sm-C^* phases are different; there exist regions of the phase diagram where solutions for both can be found.

For $H < H_{\rm LP}$ (but not too small), we always have the phase sequence Sm-$A \rightarrow$Sm-$C^* \rightarrow$Sm-$C \rightarrow$Sm-C^*, whatever the variation of q with T; that is, near the Lifshitz point, the dependence of q on T does not seem to influence qualitatively the phase diagram. This fact suggests to us that there is no relation between the maximum in the pitch (observed in DOBAMBC at $T_c - T \sim 0.5$ K) and the re-entrant phenomenon, as suggested by Muševič *et al.*[2] In fact, according to our results, the re-entrant transition appears except when D_3 is zero (it may not be physically accessible when $|D_3|$ is small), regardless of the dependence of q on H. We note that when D_3 takes on very large values, one has only the Sm-A–Sm-C^* transition (except for a very small interval near the Lifshitz point).

The Sm-C–Sm-C^* transition is first order near the Lifshitz point and becomes second order at low temperatures. In Figs. 2 and 3 the location of the tricritical point (TCP) is shown. The location of the TCP depends only weakly on D_3; for the parameter values investigated, it is always in the range $0 \leq A \leq 5$.

In Fig. 4 we show the variation of the wave number q (defined by $qL = 2\pi$ where L is the spatial period) as a function of χH^2 for different values of A, for $D_3 = 10$. We choose various values of A: (a) near T_c ($A = 2$ and $A = 0$); (b) close to the nose ($A = -2$), near the smallest value of H for which there is a re-entrant transition; (c) near the TCP, but slightly below it ($A = -3.85$); and (d) well below the tricritical point. The Sm-C–Sm-C^* transition is first order for (a) and (b), so that q is discontinuous there, and second order for (c) and (d). The prediction of the one-harmonic approximation that q^2 varies linearly with H^4 is not verified for $A = 2$. Therefore this approximation is valid only very near the Lifshitz point, in agreement with the conclusion of Ref. 7.

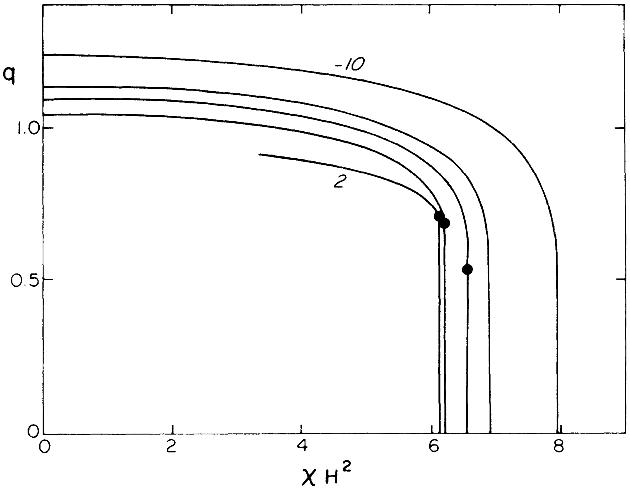

FIG. 4. The wave number q of the Sm-C^* phase as a function of χH^2 for $A = 2$, 0, -2, -3.85067, and -10. The transition from the Sm-C^* phase to the Sm-C phase is first order for the first three values of A (2, 0, and -2), and second order for the last two; the wave number is therefore discontinuous in the first three cases, and continuous in the last two (though very steep, as usual in second-order incommensurate-commensurate transitions). The other Landau parameters have the values $B_1 = 50$, $C_1 = 500$, $D_1 = 1$, $D_2 = 2$, and $D_3 = 10$. For $A = 2$, the Sm-A–Sm-C^* transition is at $\chi H^2 = 3.314$, and so q is undefined for smaller values of χH^2.

The unwinding of the helix by increasing the magnetic field, keeping T constant, is easily understood in the two extreme cases: near the Lifshitz point and at low temperatures. Michelson[3] has already analyzed the unwinding process near the Lifshitz point. In this case,

$$n_x = n_1 \cos(qz), \quad n_y = n_2 \sin(qz) . \tag{9}$$

When H increases, n_2 and q decrease, n_1 increases until the transition takes place suddenly to the Sm-C phase. At low temperatures ($A \leq -100$) the amplitude remains constant and the unwinding occurs by rotation of the molecules, while q goes to zero. However, as shown above, ϕ is far from being linearly dependent on z as near the LP. At intermediate values of A, the process is complex, since it involves the variation of n_1, n_2, and q.

An interesting case occurs when $D_2 D_3 < 0$ and the point where $q = 0$ appears for low enough values of A. Near this point, the unwinding field is low and both the one-harmonic and the constant-amplitude approximations are valid. Thus during the unwinding we have always $n_x = n \cos(qz)$ and $n_y = n \sin(qz)$, and only q varies with H.

Qualitatively, the calculated phase diagram is very similar to the experimental diagram for DOBAMBC, for example taking $D_3 = 10$. We were unable to perform a quantitative comparison, because we do not know the values of the Landau coefficients appearing in Eq. (2). Dumrongrattuna *et al.*[11] gave values of A, B_1 and C_1, but the determination of D_1, D_2, and D_3 requires measurements of both θ and q as functions of temperature.

Early measurements of the latter two quantities by different groups gave quite different values, but recent measurements[10,12] are more consistent; unfortunately we still lack a full set of measurements (preferably for the same sample of the same compound) to attempt a fit to experiment.

Figure 5 shows the evolution of the order parameter with temperature, for three sets of the Landau parameters. Note that the overall amplitudes of the order parameter are rather large (because of the particular values chosen for the Landau parameters), but can be reduced by scaling, as discussed at the beginning of this section. At high temperatures (well above the upper Sm-C–Sm-C^* transition) the two components of n are small in amplitude and are nearly sinusoidal functions of position. Unusual behavior, apparently new with the present model, is found at very low temperature (well below the lower Sm-C–Sm-C^* transition) where the components are large in magnitude (as expected), but surprisingly are again nearly sinusoidal. In other commensurate-incommensurate systems, the low-temperature phase is usually commensurate, and in the Lifshitz-invariant class of incommensurate materials, the order parameter "squares up" with decreasing temperature as the commensurate phase is approached. Here, in contrast, the low-temperature phase is incommensurate. It appears that proximity to the commensurate phase, rather than low temperature, is required for a well-developed domain structure in the Lifshitz-invariant class.

In the left column of Fig. 5, parts (a)–(d), the two Sm-C–Sm-C^* transitions are first order and the domain structure is poorly developed; the order parameter is hardly changed on going from just above the upper transition, part (b), to just below the lower, part (c). In the center column, parts (e)–(g), the upper transition is first order and the lower second order, but the latter is very near the tricritical point; part (f) shows clearly the overshooting of the amplitude discussed in Sec. VI—here the component n_x itself overshoots. In the right column, parts (h)–(j), both Sm-C–Sm-C^* transitions are second-order and the domain structure is well developed; the helicity has opposite sign in the Sm-C^* phases above and below the Sm-C phase, as shown by parts (h) and (i).

VI. INTERACTION OF DISCOMMENSURATIONS

The amplitude $n(z)$ and the phase $\phi(z)$ of the order parameter are defined by

$$\begin{aligned} n_x(z) &= n(z)\cos\phi(z) \ , \\ n_y(z) &= n(z)\sin\phi(z) \ . \end{aligned} \tag{10}$$

Early treatments of the theory of liquid crystals[13] and of incommensurate systems[14,15] used the constant-

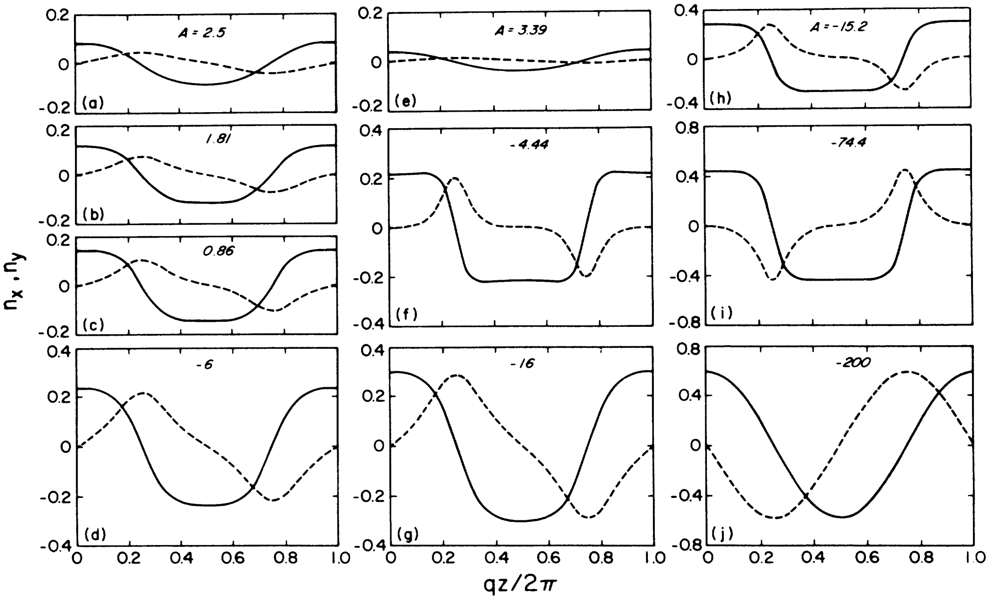

FIG. 5. Components n_x (solid lines) and n_y (dashed lines) of the order parameter as functions of the coordinate z normal to the layers, for various values of D_3, χH^2, and A; the values of the other Landau parameters are given in the caption to Fig. 2. These are the optimal functions for the given Landau parameters—the free energy is minimized with respect to q. Left column: $D_3 = 10$ and $\chi H^2 = 6.1$; both the upper and lower Sm-C–Sm-C^* transitions are first order. (a) $A = 2.5$, $q = 0.714$; (b) $A = 1.81, q = 0.716$ (just above the Sm-C phase); (c) $A = 0.86, q = 0.711$ (just below the Sm-C phase); (d) $A = -6, q = 0.989$ (well below the Sm-C phase). Center column: $D_3 = 10$ and $\chi H^2 = 7$; the upper Sm-C–Sm-C^* transition is first order, and the lower is second order. (e) $A = 3.39, q = 0.499$ (just above the Sm-C phase); (f) $A = -4.44, q = 0.488$ (just below the Sm-C phase); (g) $A = -16, q = 1.125$ (well below the Sm-C phase). Right column: $D_3 = -20$, $\chi H^2 = 1$; both the upper and the lower Sm-C–SmC^* transitions are second order. (h) $A = -15.2, q = 0.234$ (just above the Sm-C phase); (i) $A = -74.4, q = 0.222$ (just below the Sm-C phase); (j) $A = -200$, $q = 1.571$ (well below the Sm-C phase).

amplitude approximation $n(z)=n_c$, where n_c is the order parameter of the commensurate state (here the Sm-*C* state); then the Euler-Lagrange equation for the phase reduces to the sine-Gordon equation and an analytical solution for $\phi(z)$ is easily obtained, as in the classical work of Frank and Van der Merwe.[16] In this approximation, the phase is an almost linear function of z at high temperatures, but it gradually develops structure with decreasing temperature, until at temperatures just above the transition to the commensurate state it displays a staircase form; the phase is nearly constant in the commensurate regions, and varies rapidly with position in the regions between. The phase is a monotonically increasing (or decreasing) function of z, in this approximation, and the incommensurate-commensurate (Sm-C^*–Sm-C) transition is second order. One then has a domain-wall picture of the incommensurate state (at least just above the transition to the commensurate state) where the phase of the order parameter changes from one commensurate value to another; these domain walls are called discommensurations[14] in the theory of incommensurate systems.

Later treatments of incommensurate systems (particularly a charge-density-wave system with a threefold degenerate commensurate state[17–20]) took into account the spatial variation of the amplitude (as well as the phase). The amplitude was found to be depressed in the center of the discommensuration, reasonably enough, but a curious overshooting phenomenon was noted,[17] at least in some cases; the amplitude did not increase monotonically to the asymptotic (commensurate) value, but rose above it and then decreased.

The theory of the incommensurate-commensurate transition was clarified by Jacobs and Walker,[20] who showed that the approach of the amplitude to the commensurate value could be even stranger than an overshooting; the approach was not exponential, but rather an exponentially damped sinusoid, in some cases. Moreover, the phase was also not monotonic, but displayed the same exponentially damped sinusoidal behavior as the amplitude. They also showed that, in such cases, the interaction of discommensurations was attractive (rather than repulsive as in the constant-amplitude approximation) for large separations of the discommensurations, giving rise to a first-order incommensurate-commensurate transition (rather than a second-order one as in the constant-amplitude approximation).

With this background, it is easy to understand the change in the order of the Sm-C^*–Sm-C transition; recall that the transition is first-order near the Lifshitz point (as shown by Michelson[3]), but switches to second-order at lower temperatures (as predicted by the constant-amplitude approximation which is valid at very low temperatures, as we discussed previously[7]). We show in this section that the transition is first order or second order according to whether the interaction of widely separated discommensurations is attractive or repulsive; the sign of the interaction is determined by whether the asymptotic behavior of the order parameter is a pure exponential or an exponentially damped sinusoid. An explicit calculation of the asymptotic interaction of discommensurations follows.

We consider a sample (of length L in the z direction) containing N discommensurations separated by a distance $2Z=L/N$. The interaction energy of this chain of N discommensurations is obtained in the Appendix as

$$F_{\text{inter}}=4N[D_1(\tilde{n}_x\tilde{n}'_x-\tilde{n}_y\tilde{n}'_y)+(D_2+\tfrac{3}{2}D_3n_c^2)\tilde{n}_x\tilde{n}_y]_{z=Z}\ , \tag{11}$$

where Z is located midway between two discommensurations (centered at $z=0$ and $z=2Z$), $\tilde{n}_x$ and $\tilde{n}_y$ are deviations (from their commensurate values) of the components of the order parameter for a single discommensuration [see Eq. (A9)], and the primes denote differentiation with respect to z.

The above expression for the interaction energy can be evaluated at large Z and for parameter values such that the free energy of the state with a single discommensuration equals the free energy of the commensurate state. If the result is negative, then the interaction between discommensurations is attractive (more precisely, the free energy is decreased if more discommensurations are introduced), and the commensurate-incommensurate transition is first order. If the result is positive, then the transition is likely second order; Eq. (11) evaluates only the long-range interaction of discommensurations, however, and the transition can be first order even though the long-range interaction is repulsive. Only numerical solution of the differential equations can decide whether the free energy has a deep interior minimum.

But the analysis of the previous paragraph oversimplifies, for (as in Ref. 20 and here) the interaction energy can be an exponentially damped sinusoidal function of Z; in such cases, the interaction energy is negative for some values of Z, however, and the transition is first order. Different behavior yet was found in Ref. 21; see Eq. (4) there.

For the problem at hand, the first step in evaluating the interaction energy is to examine the asymptotic behavior of the order parameter in order to determine the decay constant; we therefore write

$$\begin{aligned} n_x(z)&=n_c+\mathcal{N}_xe^{-\alpha z}\ ,\\ n_y(z)&=\mathcal{N}_ye^{-\alpha z}\ . \end{aligned} \tag{12}$$

The amplitudes $\mathcal{N}_x$ and $\mathcal{N}_y$, and the decay constant α are related by

$$\begin{aligned} &\mathcal{N}_x(K_1-D_1\alpha^2)+\mathcal{N}_y\alpha(D_2+\tfrac{3}{2}D_3n_c^2)=0\ ,\\ &\mathcal{N}_x(-\alpha)(D_2+\tfrac{3}{2}D_3n_c^2)+\mathcal{N}_y(K_2-D_1\alpha^2)=0\ , \end{aligned} \tag{13}$$

where K_1 and K_2 are defined by

$$\begin{aligned} K_1&=A-\tfrac{1}{2}\chi H^2+6B_1n_c^2+15C_1n_c^4\ ,\\ K_2&=A+2B_1n_c^2+3C_1n_c^4\ . \end{aligned} \tag{14}$$

One easily finds a quadratic equation for α^2; the discriminant $\mathcal{D}$ is

$$\mathcal{D}=[-D_1(K_1+K_2)+(D_2+\tfrac{3}{2}D_3n_c^2)^2]^2-4D_1^2K_1K_2\ , \tag{15}$$

so that the decay constant α is real if $\mathcal{D} > 0$, and complex if $\mathcal{D} < 0$. In the latter case, a simple analysis shows that the interaction energy has the same form as in Ref. 20, an exponentially damped sinusoid, and hence the transition is first order if $\mathcal{D} < 0$.

The case $\mathcal{D} > 0$ (real decay constant) requires further analysis; the solution for α which gives the dominant behavior at large distances is

$$\alpha = \{[D_1(K_1+K_2) - (D_2+\tfrac{3}{2}D_3 n_c^2)^2 - \mathcal{D}^{1/2}]/(2D_1^2)\}^{1/2} . \tag{16}$$

The interaction energy then has the form

$$F_{\text{inter}} = Ce^{-2\alpha Z} , \tag{17}$$

where the coefficient C is

$$C = 4N[-\alpha D_1(\mathcal{N}_x^2 - \mathcal{N}_y^2) + (D_2 + \tfrac{3}{2}D_3 n_c^2)\mathcal{N}_x \mathcal{N}_y] . \tag{18}$$

In principle, the coefficient C can have either sign, and the transition can therefore be either first order or second order when the decay constant is real.

The sign of the corresponding coefficient for the model of Ref. 20 was considered there, but only numerically; the sign was found to be positive, thus showing that the long-range interaction is repulsive and providing strong evidence for a second-order transition (in agreement with the full numerical solution of the differential equations) when the decay constant is real (in the model of Ref. 20).

For the problem at hand, the sign of the coefficient C (in the case of a real decay constant) can be determined analytically. One obtains

$$C = 4N\mathcal{N}_y^2 \alpha \mathcal{D}^{1/2}/(K_1 - D_1\alpha^2) , \tag{19}$$

which, curiously, vanishes at $\mathcal{D}=0$; the sign of the interaction energy is therefore determined by the sign of $K_1 - D_1\alpha^2$. A simple calculation (using the expression for n_c in terms of the Landau parameters) shows that $K_1 > D_1\alpha^2$ in all cases (even when $\mathcal{D}=0$). When the decay constant is real ($\mathcal{D}>0$), the transition is therefore second order in the model considered here (unless the free energy has a deep interior minimum). Other models require separate calculations, but a similar result appears to hold for the model of Ref. 20 [the interaction energy has the same form as Eq. (11), apart from a redefinition of parameters, because only the gradient terms appear in the interaction energy and these are almost identical in the two models]; another model (see Ref. 22) has different behavior, an attractive interaction with real decay constant. But real and complex decay constants do not exhaust the possibilities; the imaginary decay constants found in Refs. 23 and 24 signal an instability of the commensurate state to ripples.

VII. SUMMARY

The inclusion of the term

$$(n_x^3 dn_y/dz - n_y^3 dn_x/dz)$$

in the free energy provides a simple explanation of two phenomena: the pitch is temperature dependent, and the Sm-C^* phase is re-entrant. Depending on the relative signs of the Landau coefficients D_2 and D_3, we find different topologies for the field-temperature phase diagram. If $D_2D_3 > 0$, the Sm-C^* phase is re-entrant only when the magnetic field is large enough, and the Sm-C–Sm-C^* line exhibits a "nose." If $D_2D_3 < 0$: the Sm-C^* phase is re-entrant for any value of the magnetic field; for $H=0$ the pitch diverges at some temperature, and the Sm-C–Sm-C^* line splits into two different lines which meet at the point where the pitch diverges. The theoretical results are in good qualitative agreement with measurements made on the compound DOBAMBC, for which it appears that $D_2D_3 > 0$. Unfortunately, presently available experimental data are insufficient to permit direct quantitative comparison with our theory.

ACKNOWLEDGMENTS

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APPENDIX

The free energy of a sample (of length L), containing a chain of N discommensurations separated by a distance $2Z = L/N$, can be written as

$$F_{\text{chain}} = F_c + N\int_{-Z}^{Z}(\mathcal{F} - \mathcal{F}_c)dz , \tag{A1}$$

where $\mathcal{F}$ is the free-energy density of Eq. (2), $\mathcal{F}_c$ is the free-energy density of the commensurate (Sm-C) state, and $F_c = L\mathcal{F}_c$ is the free energy of the commensurate state. We focus attention on a single discommensuration which is centered at the origin; the component n_x vanishes at $z=0$ and is odd about $z=0$, while the component n_y is even about $z=0$.

We assume that the discommensurations are widely separated, so that within the region $-Z$ to Z the components of the order parameter (n_x and n_y) are very nearly equal to those for a single discommensuration (n_{x0} and n_{y0}). That is, in the region $-Z \le z \le Z$, we have

$$\begin{aligned} n_x &= n_{x0} + n_{x1} , \\ n_y &= n_{y0} + n_{y1} , \end{aligned} \tag{A2}$$

where n_{x1} and n_{y1} are the perturbations to n_{x0} and n_{y0} due to the neighboring discommensurations.

Similarly, the free-energy density $\mathcal{F}$ will be perturbed from its value $\mathcal{F}_0$ (obtained from Eq. (2) by substituting n_{x0} and n_{y0} for n_x and n_y):

$$\mathcal{F} = \mathcal{F}_0 + \mathcal{F}_1 + \mathcal{F}_2 + \cdots , \tag{A3}$$

where the subscripts denote the order in the perturbations n_{x1} and n_{y1}; we shall need both $\mathcal{F}_1$ and $\mathcal{F}_2$, but not the higher-order terms. A calculation similar to that described in detail in Ref. 20 gives $\mathcal{F}_1$ and $\mathcal{F}_2$ as perfect derivatives,

$$\begin{aligned} \mathcal{F}_1 = [&2D_1(n'_{x0}n_{x1} + n'_{y0}n_{y1}) \\ &+ D_2(n_{x1}n_{y0} - n_{x0}n_{y1}) + D_3(n_{x1}n_{y0}^3 - n_{x0}^3 n_{y1})]' , \end{aligned} \tag{A4}$$

$$\mathcal{F}_2=[D_1(n_{x1}n'_{x1}+n_{y1}n'_{y1})+\tfrac{3}{2}D_3(n_{y0}^2-n_{x0}^2)n_{x1}n_{y1}]' \ . \tag{A5}$$

Next, the free energy of the chain is written as

$$F_{\text{chain}}=F_c+N(F_{\text{single}}-F_c)+F_{\text{inter}} \ , \tag{A6}$$

where F_{single} is the free energy of the sample with a single discommensuration,

$$F_{\text{single}}=F_c+\int_{-\infty}^{\infty}(\mathcal{F}_0-\mathcal{F}_c)dz \ , \tag{A7}$$

and F_{inter} is the interaction energy of the discommensurations

$$\begin{aligned}F_{\text{inter}}=&N\int_{-Z}^{Z}(\mathcal{F}_1+\mathcal{F}_2)dz\\&-N\left[\int_{-\infty}^{-Z}(\mathcal{F}_0-\mathcal{F}_c)dz+\int_{Z}^{\infty}(\mathcal{F}_0-\mathcal{F}_c)dz\right] \ .\end{aligned} \tag{A8}$$

The difference $\mathcal{F}_0-\mathcal{F}_c$ can also be written as a perfect derivative in the regions $-\infty<z<-Z$ and $Z<z<\infty$ where the components n_{x0} and n_{y0} of the order parameter for a single discommensuration are very nearly equal to their commensurate values,

$$\begin{aligned}n_{x0}&=n_{xc}+\tilde{n}_x \ ,\\ n_{y0}&=n_{yc}+\tilde{n}_y \ ,\end{aligned} \tag{A9}$$

where $\tilde{n}_x$ and $\tilde{n}_y$ are the deviations of n_x and n_y from the commensurate values; note that n_{xc} is a function of z, and odd in z (say $n_{xc}=n_c$ for $z=-Z$ and $n_{xc}=-n_c$ for $z=Z$), and that $n_{yc}=0$. A calculation similar to that of Ref. 20 gives $\mathcal{F}_0-\mathcal{F}_c$, to second order in the deviations, as a perfect derivative.

$$\begin{aligned}\mathcal{F}_0-\mathcal{F}_c=&[-D_2(n_{xc}\tilde{n}_y-n_{yc}\tilde{n}_x)-D_3(n_{xc}^3\tilde{n}_y-n_{yc}^3\tilde{n}_x)]'\\&+[D_1(\tilde{n}_x\tilde{n}'_x+\tilde{n}_y\tilde{n}'_y)\\&+\tfrac{3}{2}D_3(-n_{xc}^2+n_{yc}^2)\tilde{n}_x\tilde{n}_y]' \ .\end{aligned} \tag{A10}$$

These manipulations have obtained the free energy of the chain to second order in small quantities (the perturbations n_{x1} and n_{y1}, and the deviations $\tilde{n}_x$ and $\tilde{n}_y$) evaluated at points midway between discommensurations.

Using the symmetry properties of the perturbations and the deviations, for example $n_{x1}(-Z)=-n_{x1}(Z)$, and the following relations for the perturbations in terms of the deviations:

$$\begin{aligned}n_{x1}(Z)&=\tilde{n}_x(Z) \ ,\\ n_{y1}(Z)&=-\tilde{n}_y(Z) \ ,\end{aligned} \tag{A11}$$

we obtain Eq. (11) for the interaction energy of the chain of discommensurations.

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