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Steric model for the smectic-*C* phase

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A steric model of the smectic-*C* phase is presented, with molecules assumed to have a symmetric zig-zag shape (this kind of molecular gross shape may arise from obliquely placed end chains). The interaction between such molecules depends on mixed tensors $\vec{\nu}^3 \vec{\nu}^2$, etc., as well as on the usual tensors $\vec{\nu}^3\vec{\nu}^3$, $\vec{\nu}^2\vec{\nu}^2$, and similar higher-order tensors, where $\vec{\nu}^3$ and $\vec{\nu}^2$ are unit vectors denoting the directions of the long molecular axis and a transverse axis, respectively. A simple interaction, which includes a term that mimics the effect of the zig-zag shape, is constructed in terms of these tensors. Using quite plausible values for the magnitude of the zig-zag part of the interaction, a second-order phase transition to a smectic-*C* phase is found, characterized by nonvanishing values of biaxial order parameters $\langle \vec{\nu}^3\vec{\nu}^2 \rangle$, etc. In the limit of perfect nematic order, the biaxial order parameters of the model are essentially equivalent to the vector order parameters used by de Gennes and by McMillan. The smectic planar structure is accounted for in the simple density-wave approximation of Kobayashi and McMillan. Only one phase with more orientational order than the smectic-*A* phase is obtained; this is in contrast to McMillan's dipole model, which shows three different ordered phases (one of which corresponds to the smectic-*C* phase). The present model predicts that the characteristic biaxialities in the smectic-*C* phase may easily grow up to values of $O(10^{-1})$.

I. INTRODUCTION

This paper presents a "steric" model of the smectic-*C* phase. An effective interaction is written down which takes into account, at least qualitatively, the packing requirements of zig-zag–shaped molecules. The molecules are also assumed to be symmetric, i.e., to have a center of symmetry, a property which seems to be common to all the known smectic-*C* materials.[1] The interaction between such molecules is unchanged by the combined operation $\vec{\nu}^3(\alpha) \rightarrow -\vec{\nu}^3(\alpha)$, $\vec{\nu}^2(\alpha) \rightarrow -\vec{\nu}^2(\alpha)$ (reversal of molecular axes 3 and 2 of molecule α), but not by the first or second operation alone. (In the following, $\vec{\nu}^3$ denotes the unit vector along the direction of the long molecular axis and $\vec{\nu}^2$ that along a transverse axis; in the nematic phase the average direction of $\vec{\nu}^3$ determines the nematic axis.) It follows that the orientational Hamiltonian depends on mixed tensors $\vec{\nu}^3(\alpha)\vec{\nu}^2(\alpha)$, etc., as well as on the usual tensors $\vec{\nu}^3(\alpha)\vec{\nu}^3(\alpha)$, etc.,[2] and the possibility arises of nonvanishing averages like $\langle \vec{\nu}^3\vec{\nu}^2 \rangle$. In fact, according to the model presented below, the transition from the smectic-*A* to the smectic-*C* phase occurs when such averages become nonvanishing.

As described in Sec. II, the zig-zag gross shape of the molecules is thought to be a result of, most likely, end chains symmetrically attached to the molecules. The increased stability of the smectic-*C* phase for higher members of a homologous series of compounds is one experimental hint suggesting that end chains play an important role in the formation of the smectic-*C* phase.

In our model the planar structure of the smectic phase is included within the simple density-wave approximation of McMillan[3] and Kobayashi.[4] In this respect the theoretical treatment presented here is an improvement on the essentially two-dimensional calculation of McMillan[1] in his electric-dipole model for the smectic-*C* phase; it should be easy to apply our treatment to that model also.

The tilt angle χ appears in the model like a geometric parameter of the system, and is in this way similar to the pitch q (or rather qa, a being a molecular length) in a cholesteric liquid crystal[5] (see Appendix B). Thus, as in McMillan's model, χ is a secondary quantity which is a function of the characteristic order parameters of the smectic-*C* phase, but not itself an order parameter. In de Gennes's Landau theory,[6] on the other hand, the tilt angle χ is taken as a primary quantity. Of course, if one is interested in χ only, then it is always possible to construct a phenomenological theory with χ as the primary quantity (eliminating all the order parameters μ in favor of χ from the equilibrium equations $\partial F/\partial \mu = 0$, where F is the free energy).

A result of the model is the prediction that the orientational order in the smectic-*C* phase is biaxial—the transverse axis $\vec{\nu}^2$, say, prefers to be in the tilting plane rather than normal to it. This anisotropy perpendicular to the nematic axis grows continuously from zero at the $A \rightarrow C$ phase transition. The same result is obtained in McMillan's model and, probably, in any molecular model of the smectic-*C* phase; the tilting plane (which is a plane of reflection symmetry) breaks the uniaxial symmetry of the molecular environment in the smectic-*C* phase just as the pitch axis breaks it in cholesteric liquid crystals (see also Sec. VI).[5,7]

The steric model exhibits only *one* second-order phase transition from the smectic-*A* phase to the more ordered smectic-*C* phase. This is in contrast with the dipole model of McMillan, which shows three different ordered phases below the smectic-*A* phase (one of which corresponds to the smectic-*C* phase).[1]

II. DESCRIPTION OF MODEL

We assume that the molecules of the system possess a symmetric zig-zag shape (in addition to being elongated—along the axis $\vec{\nu}^3$—as are all liquid-crystal-forming molecules). The zig-zag shape is most likely to result from end chains, not collinear with the central body of the molecule, as in the compounds *n*-heptyloxy azoxy benzene.[1] A similar effect, from the point of view of the problem of packing molecules, may perhaps also be produced by symmetrically placed side chains (Fig. 1). As mentioned in the introduction, the smectic-*C* phase seems to occur only in symmetric compounds.

The possibility that alkyl end chains placed aslant on the molecule may be crucial for the formation of the smectic-*C* phase has been recognized by Wise, Smith, and Doane.[8] However, they tentatively ruled out this possibility on the basis of their nuclear-magnetic-resonance experiment in terephal-bis-4 (4 *n*-butylaniline). It seems to us that the question is still open; the biaxialities are small for small tilt angles (see Sec. V) and, further, may have only a small effect on the observed nuclear-magnetic-resonance line shape.[9]

McMillan has argued that the zig-zag shape of the molecule may be helpful in increasing the stability of the smectic-*C* phase.[1]

The point of view represented in this paper is that the repulsive, or steric, forces play a predominant role in liquid crystals,[10] just as in simple liquids.[11] That is, the characteristic orientational order which distinguishes a mesophase from ordinary liquids is assumed to be mainly a result of the effect of molecular shape on the packing problem for the liquid. (In the case of the smectic *density wave,* on the other hand, it appears that attractive and repulsive forces are equally important—the repulsive forces in defining a nematic axis and the attractive forces in favoring a density wave along that axis.)

We write down a simple effective interaction between molecules which will mimic, at least qualitatively, the effect of the molecular zig-zag shape; this interaction is then used in a standard mean-field calculation (complicated somewhat by the presence of the smectic density wave). This program is in the same spirit as some previous work on a very simple model for cholesteric liquid crystals.[12]

The "zig-zag interaction" between a pair of molecules 1 and 2 is taken to be

$$-A_1(r)[\vec{\nu}^3(1)\cdot\vec{\nu}^3(2)][\vec{\nu}^2(1)\cdot\vec{\nu}^2(2)]$$

$$-[A_2(r)/r_2^2][\vec{\nu}^3(1)\cdot\overrightarrow{\mathrm{r}\nu}^2(1)\cdot\vec{\mathrm{r}}+\vec{\nu}^3(2)\cdot\overrightarrow{\mathrm{r}\nu}^2(2)\cdot\vec{\mathrm{r}}]\ . \qquad (1)$$

The first term accounts for the fact that the molecules interfere less with one another if their long *and* short axes align together. The second term represents the additional tendency of the molecules to tilt over with respect to their intermolecular vector $\vec{\mathrm{r}}$ in order to achieve optimum packing (Fig. 1); r_2 is the range of $A_2(r)$. This interaction is invariant under the operation $\vec{\nu}^3\rightarrow-\vec{\nu}^3$, $\vec{\nu}^2\rightarrow-\vec{\nu}^2$ applied to either one of the molecules, as required for symmetric molecules (Sec I). A criticism that may be made of form (1) is that the second term favors tilting even if the long and short axes of 1 and 2 are not approximately aligned; however, by choosing $0<A_2(r)\ll A_1(r)$ this unphysical feature of (1) should become unimportant. The choice

$$0<A_2(r)<\tfrac{1}{4}A_1(r) \qquad (2)$$

is convenient. Correcting the second term of (1) by a factor which is large only when molecules 1 and 2 are appropriately aligned would complicate the model (by requiring the introduction of molecular tensors $\nu_i\nu_j\cdots\nu_l\nu_m$ and corresponding order parameters of order higher than 2) without essentially modifying the qualitative behavior of the sum (1) (provided $A_2<A_1$).

The total effective orientational Hamiltonian is taken to be

$$H=H_n+H_{sa}+H_{sc}\ , \qquad (3)$$

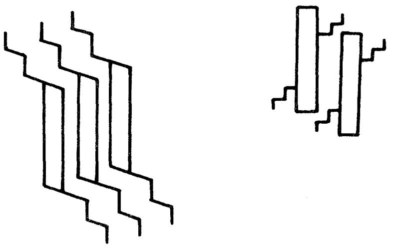

FIG. 1. Schematic representation of two examples of zig-zag molecular shapes. Jagged lines represent semi-flexible chains.

where

$$H_n = -\tfrac{1}{2}\sum_{\alpha\neq\beta} \tfrac{3}{2}A_0(r)\overleftrightarrow{\mathrm{Q}}(\alpha):\overleftrightarrow{\mathrm{Q}}(\beta)\,, \tag{4a}$$

$$H_{sc} = -\tfrac{1}{2}\sum_{\alpha\neq\beta}\left(A_1(r)\overleftrightarrow{\mathrm{R}}(\alpha):\overleftrightarrow{\mathrm{R}}^T(\beta) + \frac{A_2(r)}{r_2^2}\vec{\mathrm{r}}\cdot\left[\overleftrightarrow{\mathrm{R}}(\alpha)+\overleftrightarrow{\mathrm{R}}(\beta)\right]\cdot\vec{\mathrm{r}}\right), \tag{4b}$$

$$\vec{\mathrm{r}} = \vec{\mathrm{r}}_\alpha - \vec{\mathrm{r}}_\beta,\quad \overleftrightarrow{\mathrm{Q}}(\alpha) = \vec{\nu}^3(\alpha)\vec{\nu}^3(\alpha) - \tfrac{1}{3}\overleftrightarrow{1}\,, \qquad \overleftrightarrow{\mathrm{R}}(\alpha) = \vec{\nu}^3(\alpha)\vec{\nu}^2(\alpha)\,. \tag{4c}$$

The superscript "T" denotes matrix transpose. H_n is the usual nematic term,[13] and H_{sc} is the zigzag interaction. H_{sa} is a term present also in substances having just a smectic-A phase and no smectic-C phase; it favors keeping the axes $\vec{\nu}^3$ of the molecules normal to the smectic planes. H_{sa} may contain terms proportional to $\vec{\mathrm{r}}\cdot\overleftrightarrow{\mathrm{Q}}(\alpha)\cdot\overleftrightarrow{\mathrm{Q}}(\beta)\cdot\vec{\mathrm{r}}$, for example. Both H_{sa} and H_{sc} are expected to be small compared to H_n. The main effect of H_{sa} is to contribute to the free energy a positive term proportional to χ^2 (for small values of tilt angle χ),

$$\langle H_{sa}\rangle = C_{1a}\chi^2\,, \tag{5}$$

where C_{1a} is a function of the smectic-A order parameters (see Sec. IV). It should be noted that, in general, H_n also contributes a term proportional to χ^2 to the free energy. This is calculated in Appendix A for the case that the system is kept at constant volume.

The most convenient choice for the functions $A_m(r)$ appearing in Eqs. (4) is the Gaussian form[3]

$$A_m(r) = (V_m/\rho\pi^{3/2}r_m^3)e^{-r^2/r_m^2} \quad (m=0,1,2)\,, \tag{6}$$

where $V_m \geqslant 0$ is an interaction strength with dimensions of energy and ρ is the number density of the system. It is useful to define parameters α_m and $\overline{\alpha}_m$ connected with the functions $A_m(r)$,

$$\alpha_m = 2e^{-(\pi r_m/d)^2},\quad \overline{\alpha}_m = (\pi r_m/d)^2\alpha_m\,. \tag{7}$$

d is the wavelength of the smectic density wave in the direction of the nematic axis.

III. SMECTIC PLANES AND ZIG-ZAG INTERACTION

To define a tilt angle χ the system must possess another axis Z' besides the nematic axis Z associated with the orientational order. The normal to the smectic planes in smectic liquid crystals provides the required axis of reference Z'. The system is assumed to be kept at constant volume.

In Appendix A it is shown that the contribution of H_n to the mean field U is, to second order in χ,

$$U_n(\chi;\,\theta_1,\zeta_1) = U_n(\theta_1,\zeta_1) + \tfrac{3}{2}Q_{33}(1)\cos(2\pi\zeta_1/d)\sigma\chi^2V_0\overline{\alpha}_0\,, \tag{8}$$

where $U_n(\theta_1,\zeta_1)$ is McMillan's mean field for the smectic-A phase. In terms of the coordinates z, y defined by the nematic axis Z and its perpendicular companion Y (the axes Z', Z, Y are coplanar, see Fig. 2) we have

$$\zeta = z - y\tan\chi\,. \tag{9}$$

The order parameter σ is

$$\sigma = \langle\tfrac{3}{2}Q_{33}(1)\cos 2\pi\zeta_1/d\rangle\,. \tag{10}$$

Throughout this paper the brackets $\langle\,\rangle$ denote the mean-field average defined by

$$\langle f(\Omega,\zeta)\rangle = \frac{1}{d}\int_0^d d\zeta\int d\Omega\, h(\Omega,\zeta)f(\Omega,\zeta)\,,$$

$$h(\Omega,\zeta) = (1/Z_1)e^{-\beta U(\Omega,\zeta)}$$

$$Z_1 = \frac{1}{d}\int_0^d d\zeta\int d\Omega\, e^{-\beta U(\Omega,\zeta)}\,.$$

Ω stands for the Euler angles of a molecule measured in the tilted frame X, Y, Z, and β is the inverse product of the absolute temperature T and the Boltzmann constant k_B. The molecular distribution function

$$\rho(\Omega,\zeta) = \rho h(\Omega,\zeta)$$

is, of course, periodic in ζ, Eq. (9), with the period d (distance between smectic planes is $d\cos\chi$).

Next we consider the contribution to U of the zigzag interaction H_{sc}. This contribution, denoted by U_c, contains terms linear in χ and is responsible for the phase transition $\chi = 0$ (smectic A) → $\chi > 0$ (smectic C). For simplicity, U_c is evaluated only up to the important linear terms in χ (we consider only small χ, $\chi \leqslant 10^{-1}$ rad $\approx 5°$). This means that the shifting of the mass centers as χ increases at constant volume (see Appendix A) can be neglected; i.e., we can put

$$\zeta = z'/\cos\chi \approx z'\,, \tag{11}$$

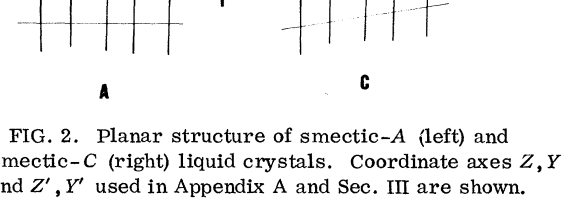

FIG. 2. Planar structure of smectic-A (left) and smectic-C (right) liquid crystals. Coordinate axes Z, Y and Z', Y' used in Appendix A and Sec. III are shown.

in calculating U_c.

U_c may be conveniently written as the sum of three terms. The first term is the biaxial aligning term $U_{c,0}$:

$$U_{c,0}(\Omega_1, \zeta_1) = -R_{ij}(1) \int d^3r_2 \times \int d\Omega_2\, \rho(\Omega_2, \zeta_2) R_{ij}(2) A_1(r)\,,$$

where $\vec{r} = \vec{r}_1 - \vec{r}_2$. Following the same procedure as in Appendix A and using approximation (11), the above integral becomes

$$V_1 \frac{1}{d} \int_0^d d\zeta_2 \int d\Omega_2\, h(\Omega_2, \zeta_2) R_{ij}(2) \times \left(1 + \alpha_1 \cos\frac{2\pi\zeta_2}{d} \cos\frac{2\pi\zeta_1}{d}\right)\,,$$

so that

$$U_{c,0}(\Omega_1, \zeta_1) \simeq -R_{ij}(1)[\langle R_{ij}\rangle + \cos(2\pi\zeta_1/d) \times \langle R_{ij} \cos 2\pi\zeta/d\rangle \alpha_1] V_1\,. \tag{12}$$

Note that the presence of the smectic planes enhances the biaxial aligning influence of H_{sc}. This effect is quite important since V_1 is certainly significantly smaller than V_0.

The remaining two terms of U_c, coming from the second part of H_{sc}, are tilting terms. One of these terms is

$$U_{c,1} = -\frac{1}{r_2^2} \int d^3r_2 \int d\Omega_2\, \rho(\Omega_2, \zeta_2) \vec{r}\vec{r} : \overleftrightarrow{R}(2) A_2(r)\,.$$

This again is reduced following the method of Appendix A and using approximation (11)

$$\begin{aligned} U_{c,1} \simeq & -\frac{V_2}{\pi^{1/2} r_2}\left(\int d\zeta_2 \int d\Omega_2 h(\Omega_2, \zeta_2) \times e^{-\zeta^2/r_2^2} \overleftrightarrow{R}(2)\right) : \tfrac{1}{2}(\hat{x}'\hat{x}' + \hat{y}'\hat{y}') \\ & - \frac{V_2}{\pi^{1/2} r_2}\left(\frac{r_2}{2}\frac{\partial}{\partial r_2} \int d\zeta_2 \times \int d\Omega_2\, h(\Omega_2 \zeta_2) e^{-\zeta^2/r_2^2} \overleftrightarrow{R}(2)\right) : \hat{z}'\hat{z}' \\ & = V_2 \bar{\alpha}_2 \cos\left(\frac{2\pi\zeta_1}{d}\right) \langle \overleftrightarrow{R}(2) \cos(2\pi\zeta_2/d)\rangle : \hat{z}'\hat{z}'\,, \end{aligned} \tag{13}$$

since $\overleftrightarrow{R} : \overleftrightarrow{1} = \vec{\nu}^3 \cdot \vec{\nu}^2 = 0$. Here $\hat{x}'$, $\hat{y}'$, $\hat{z}'$ are unit vectors along the axes X', Y', $Z' = X$, Y', Z' (Fig. 2),

$$\hat{z}' = \hat{z} \cos\chi - \hat{y} \sin\chi\,.$$

Expressed in the frame X, Y, Z, Eq. (13) becomes, to first order in χ,

$$\begin{aligned} U_{c,1} & \simeq \cos(2\pi\zeta_1/d)(\langle R_{33} \cos(2\pi\zeta/d)\rangle - \chi\langle (R_{32} + R_{23}) \cos(2\pi\zeta/d)\rangle) V_2 \bar{\alpha}_2 \\ & \equiv U_{c,1}^0 - \chi U_{c,1}^1\,, \end{aligned} \tag{14}$$

where $R_{33} = \hat{z} \cdot \overleftrightarrow{R} \cdot \hat{z}$, etc.

In a similar way one obtains the other tilting term, $U_{c,2}$,

$$\begin{aligned} U_{c,2} & \simeq \{R_{33}(1) - \chi[R_{32}(1) + R_{23}(1)]\} \times \cos(2\pi\zeta_1/d) \langle \cos 2\pi\zeta_2/d\rangle V_2 \bar{\alpha}_2 \\ & \equiv U_{c,2}^0 - \chi U_{c,2}^1\,. \end{aligned} \tag{15}$$

The essential approximation involved in expressions (12), (14), and (15) is the neglect of Fourier components higher than $\cos 2\pi z/d$ of the interaction function e^{-z^2/r_m^2} [or rather, of the distribution function $\zeta(\theta, z)$]. This is done for simplicity, following McMillan[3] and Kobayashi.[4]

The total mean field acting on a molecule at $\zeta_1 = z_1 - y_1 \tan\chi$ is

$$U(\Omega_1, \zeta_1) = U_n(\theta_1, \zeta_1) + U_{c,0}(\Omega_1, \zeta_1) + \sum_{r=1}^{2} U_{c,r}^0 + \chi^2 U_a(\theta_1, \zeta_1) - \chi \sum_{r=1}^{2} U_{c,r}^1\,, \tag{16}$$

where

$$\chi^2 U_a = [U_n(\chi; \theta_1, \zeta_1) - U_n(\theta_1, \zeta_1)] + (\text{contribution from } H_{sa})\,. \tag{17}$$

In addition to σ, another smectic-A order parameter σ_0 has appeared above,

$$\sigma_0 = \langle \cos 2\pi\zeta/d\rangle\,. \tag{18}$$

The Maier and Saupe[13] order parameter for the nematic phase is denoted by η,

$$\eta = \langle \tfrac{3}{2} Q_{33}(1)\rangle\,. \tag{19}$$

IV. ORDER PARAMETERS IN SMECTIC-C PHASE

The tilt angle χ appears like an external field in U, Eq. (16). As shown in Appendix B, this means that χ satisfies

$$0 = \frac{\partial\langle U\rangle}{\partial\chi} = 2\chi\langle U_a\rangle - \left\langle \sum_1^2 U_{c,r}^1 \right\rangle\,. \tag{20}$$

By Eqs. (8), (17), and (5) we have, for the system kept at constant volume,

$$\langle U_a\rangle = V_0\bar{\alpha}_0\sigma^2 + C_{1a}(\eta, \sigma, \sigma_0, \ldots) \equiv C_1(\eta, \sigma, \sigma_0, \ldots)\,. \tag{21}$$

C_1 is an elastic constant of the smectic-*A* phase. It depends on the order parameters $\eta, \sigma, \sigma_0, \ldots$, which may be considered constant near the transition to the smectic-*C* phase.

From Eqs. (14), (15), and (18) we have

$$\left\langle \sum_1^2 U^1_{c,r}\right\rangle = 2\bar{V}_2\sigma_0\tau_1\,, \tag{22}$$

where

$$\tau_1 = \langle (R_{32}+R_{23})\cos 2\pi\zeta/d\rangle \tag{23}$$

is an order parameter peculiar to the smectic-*C* phase (obviously $\tau_1 = 0$ in uniaxial smectic-*A* phase), and $\bar{V}_2 = V_2\bar{\alpha}_2$. Combining Eqs. (20)–(22) we have

$$\chi = (\bar{V}_2\sigma_0/C_1)\tau_1\,. \tag{24}$$

The mean field U, Eq. (16), is quite complicated. Before proceeding further we note some simplifying features. First, any order parameter $F_{ij} = \langle R_{ij} f(Q_{33}, \zeta)\rangle$ with one of $i \neq j$ equal to 1 vanishes, since the plane ZY is a plane of symmetry. Further, $|F_{ij}| \ll |F_{3j}|$ for $i \neq 3$, if we assume that the nematic order is well established (so that the $\vec{\nu}^3$ axis of a molecule has small probability of deviating far from the Z axis). To keep the calculations reasonably simple we neglect the F_{ij} with $i \neq 3$. The contribution U_c of the zig-zag interaction to the mean field becomes then, from Eqs. (12), (14), and (15),

$$\begin{aligned} U_c(1) \simeq -V_1[\mu(\Omega_1)\mu + \tau(\Omega_1, \zeta_1)\tau \\ + \mu_1(\Omega_1)\mu_1 + \tau_1(\Omega_1, \zeta_1)\tau_1] \\ + \bar{V}_2\{\sigma_0(\zeta_1)[\tau - \chi\tau_1] \\ + [\tau(\Omega_1, \zeta_1) - \chi\tau_1(\Omega_1, \zeta_1)]\sigma_0\}\,, \end{aligned}$$

where the convention $\Sigma = \langle\Sigma(\Omega, \zeta)\rangle$, for any function $\Sigma(\Omega, \zeta)$, has been introduced as well as the notation

$$\mu(\Omega_1) = R_{33}(1), \quad \tau(\Omega_1, \zeta_1) = R_{33}(1)\cos 2\pi\zeta_1/d, \tag{25}$$

$$\mu_1(\Omega_1) = R_{32}(1), \quad \tau_1(\Omega_1, \zeta_1) = R_{32}(1)\cos 2\pi\zeta_1/d\,.$$

The functions $\mu(\Omega_1)$ and $\tau(\Omega_1, \zeta_1)$ are even under the transformation $\nu_2^2 \to -\nu_2^2$ ($\nu_2^2 = \vec{\nu}^2\cdot\hat{y}$), and the corresponding averages μ and τ are nonvanishing in the smectic-*A* phase [but small since $R_{33}(1) = 0$ for a molecule with $\vec{\nu}^3 = z$]. μ and τ are not expected to vary significantly near the transition to the smectic-*C* phase, and the associated terms in the mean field may be collected with $U_n(\theta, \zeta)$ into a term $U_0(\Omega, \zeta)$, which is supposed known,

$$\begin{aligned} U = U_0 + \chi^2 U_a - V_1[\mu_1\mu_1(\Omega_1) + \tau_1\tau_1(\Omega_1, \zeta_1)] \\ - \chi\bar{V}_2[\tau_1\sigma_0(\zeta_1) + \sigma_0\tau_1(\Omega_1, \zeta_1)]\,. \end{aligned} \tag{26}$$

Both U_0 and U_a have uniaxial symmetry (with symmetry axis Z). In the smectic-*A* phase only U_0 exists.

V. SMECTIC-*A*–SMECTIC-*C* PHASE TRANSITION

A. Equilibrium equations

The mean-field approximation to the free energy per molecule F for the system with the mean field (26) is given by (see Appendix B)

$$\begin{aligned} \beta F &= \beta[\tfrac{1}{2}U_1 - TS_1] = -\tfrac{1}{2}\beta U_1 + \beta F_1 \\ &= -\tfrac{1}{2}\beta\,\langle U_0\rangle - \tfrac{1}{2}\beta\chi^2 C_1 + \tfrac{1}{2}K_1(\mu_1^2 + \tau_1^2) + \chi\bar{K}_2\sigma_0\tau_1 - \ln Z_1 V\,, \end{aligned} \tag{27}$$

where U_1, S_1, and F_1 are the energy, entropy, and Helmholtz free energy of a molecule in the single-particle potential (26);

$$K_1 = \beta V_1, \quad \bar{K}_2 = \beta\bar{V}_2\,,$$

and V is the (fixed) volume of the system (Z_1 has been defined in Sec. III).

It is easy to see that the equilibrium conditions $\partial F/\partial\mu_1 = \partial F/\partial\tau_1 = \partial F/\partial\chi = 0$ lead to the self-consistency equations

$$\mu_1 = \langle\mu_1(\Omega)\rangle\,, \tag{28a}$$

$$\tau_1 = \langle\tau_1(\Omega, \zeta)\rangle\,, \tag{28b}$$

$$\chi = (\bar{V}_2\sigma_0/C_1)\langle\tau_1(\Omega, \zeta)\rangle\,. \tag{28c}$$

(Here the self-consistency equation for σ_0, $\sigma_0 = \langle\sigma_0(\zeta)\rangle$ has been assumed. The variation of σ_0 near the transition $A \to C$ is unimportant and may be neglected.)

The free energy (27) is unchanged by the transformation $\mu_1, \tau_1, \chi \to -\mu_1, -\tau_1, -\chi$ (which corresponds to a rotation of the system about the Z axis by 180°). Therefore a second-order phase transition $\chi = 0 \to \chi > 0$ is expected. In fact, in the limit of perfect nematic and smectic order considered in Appendix C it is easy to show that the phase transition must be second order. Accordingly, we look for solutions of Eqs. (28) with μ_1, τ_1, χ small.

Substituting (28b) into (28c) gives

$$\chi = (\bar{V}_2\sigma_0/C_1)\tau_1 \equiv \gamma\tau_1\,. \tag{29}$$

Expanding Z_1 for small values of μ_1, τ_1, χ, and using Eqs. (29) and (21) one gets, neglecting terms of fourth and higher order,

$$Z_1 \simeq Z_1^0[1 + \tfrac{1}{2}(K_1^2 a_{20}\mu_1^2 + 2K_1K_1^+ a_{11}\mu_1\tau_1 + K_1^{+\,2} a_{02}\tau_1^2)]\,, \tag{30}$$

where Z_1^0 is the smectic-A value of Z_1 corresponding to just the term U_0 of the mean field U, Eq. (26), and the quantities

$$a_{mn}=\frac{1}{Z_{1d}^0}\int_0^d d\zeta\int d\Omega\, e^{-\beta U_0}[\mu_1(\Omega)]^m[\tau_1(\Omega,\zeta)]^n \tag{31}$$

are smectic-A averages. Also, $K_1^+=\beta V_1^+$, where

$$V_1^+=V_1+\overline{V}_2^2\sigma_0^2/C_1\,. \tag{32}$$

Multiplying Eq. (28a) by Z_1 and expanding $(1/d)\times\int e^{-\beta U}\mu_1(\Omega)$ to third order in μ_1, τ_1, χ, one obtains, with the help of Eq. (29),

$$\begin{aligned}0\simeq{}&(1-K_1a_{20})\mu_1-K_1^+a_{11}\tau_1+\tfrac{1}{2}K_1^2(a_{20}-\tfrac{1}{3}K_1a_{40})\mu_1^3\\&+K_1K_1^+(a_{11}-\tfrac{1}{2}K_1a_{31})\mu_1^2\tau_1\\&+[K_1^{+2}\tfrac{1}{2}(a_{02}-K_1a_{22})-K_1D_{20}]\\&\times\mu_1\tau_1^2-(K_1^{+3}\tfrac{1}{6}a_{13}+K_1^+D_{11})\tau_1^3\,.\end{aligned} \tag{33}$$

The quantities D_{mn} are defined by

$$\begin{aligned}&D_{mn}=\langle[\mu_1(\Omega)]^m[\tau_1(\Omega,\zeta)]^nD\rangle_0\,,\\&D=\gamma\overline{K}_2\sigma_0(\zeta)-\gamma^2\beta U_a(\Omega,\zeta)\,,\end{aligned} \tag{34}$$

where the symbol $\langle\ \rangle_0$ means a smectic-A average—the same average with the mean field U_0 as in definition (31) of the quantities a_{mn}. Similarly, another equation is derived starting from Eq. (28b); this equation can be obtained from Eq. (33) by two sets of replacements: (a) In the terms prefixed with a plus sign replace *one* factor of μ_1 by τ_1; (b) in the terms prefixed with a minus sign replace a_{mn}, $D_{m,n}$ by $a_{m-1,n+1}$, $D_{m-1,n+1}$, respectively.

It may be checked that in the limit of perfect nematic and smectic order used in Appendix C (when $\tau_1\sim\mu_1$, $a_{m,n}\sim a_{m+n,0}$ $D_{mn}\simeq 0$, and $a_{m,0}\simeq I_m/I_0$) Eq. (33) reduces to the first two terms of (C10).

B. Critical temperature

At temperatures just below the phase transition $\mu_1, \tau_1\simeq 0$ and the following pair of homogeneous linear equations must be satisfied:

$$(1-K_1a_{20})\mu_1-K_1^+a_{11}\tau_1=0\,, \tag{35a}$$

$$-K_1a_{11}\mu_1+(1-K_1^+a_{02})\tau_1=0\,. \tag{35b}$$

Equation (35a) is the linear part of the expansion (33) of Eq. (28a), and (35b) is the linear part of the corresponding expansion of Eq. (28b). Therefore the critical temperature is fixed by the requirement that the determinant of the coefficients in Eqs. (35) be zero,

$$K_1K_1^+d-(K_1a_{20}+K_1^+a_{02})+1=0\,, \tag{36}$$

where

$$d=a_{20}a_{02}-a_{11}^2\,.$$

With the notation

$$s=a_{20}+e'a_{20}\,,\quad e'=1+\overline{V}_2^2\sigma_0^2/V_1C_1$$

(so that $K_1^+=K_1e'$), the solution of (36) for $d=0$ is

$$K_1=1/s\,. \tag{37}$$

In the case of Appendix C, $a_{20}=a_{02}=\frac{1}{2}$, and (37) becomes $K_1=1/e$, in agreement with Eq. (C11). For general d the required solution of (36) is

$$K_{1c}=\frac{s-(s^2-4e'd)^{1/2}}{2e'd}\,. \tag{38}$$

[This reduces to Eq. (37) for $|4e'd/s^2|\ll 1$.]

C. Solution for order parameters

In the limit $K_1\to K_{1c}$, Eqs. (35) hold and

$$\mu_1/\tau_1=K_{1c}^+a_{11}/(1-K_{1c}a_{20})=(1-K_{1c}^+a_{02})/K_{1c}a_{11}\equiv f_0\,. \tag{39}$$

Since $\sigma_0>0$, it is clear that μ_1 and τ_1 have the same sign [this can also be seen from the free energy (27) and Eq. (30)]; therefore $K_{1c}<1/a_{20}$, which provides another argument for the choice (38)—the smaller root of Eq. (36). We now try the solution

$$\mu_1=(f_0+f')\tau_1,\quad f'=0(\tau_1^2)\,. \tag{40}$$

Substitution of Eqs. (40) into Eq. (33) and into the similar expanded form of Eq. (28b) gives

$$\begin{aligned}&(1-K_1a_{20})(f_0+f')-K_1^+a_{11}+F_1\tau_1^2=0\,,\\&(1-K_1^+a_{02})-K_1a_{11}(f_0+f')+F_2\tau_1^2=0\,,\end{aligned} \tag{41}$$

to second order in τ_1. The coefficient F_1 is

$$\begin{aligned}F_1={}&\tfrac{1}{2}f_0^3K_1^2(a_{20}-\tfrac{1}{3}K_1a_{40})+f_0^2K_1K_1^+(a_{11}-\tfrac{1}{2}K_1a_{31})\\&+f_0K_1^{+2}(a_{02}-K_1a_{22}-2K_1D_{20}/K_1^{+2})\\&-(\tfrac{1}{6}K_1^{+3}a_{13}+K_1^+D_{11})\end{aligned}$$

F_2 can be obtained from F_1 by replacing (a) in terms prefixed with a plus sign *one* f_0 by 1 and (b) in terms prefixed with a minus sign $a_{mn}\to a_{m-1,n+1}$ and $D_{m,n}\to D_{m-1,n+1}$. Eliminating f' from Eqs. (41) gives

$$\begin{aligned}&K_1a_{11}[(1-K_1a_{20})f_0-K_1^+a_{11}]\\&\quad+(1-K_1a_{20})[(1-K_1^+a_{02})-K_1a_{11}f_0]\\&\qquad+[K_1a_{11}F_1+(1-K_1a_{20})F_2]\,\tau_1^2=0\,.\end{aligned} \tag{42}$$

For small $\Delta K=K_1-K_{1c}$ $(\Delta K/K_{1c}\simeq-\Delta T/T_c\simeq\Delta K^+/K_{1c}^+)$ the zero-order terms in (42) reduce to

$(K_{1c}f_0+K^+_{1c}f_0^{-1})a_{11}\Delta T/T_c$, so that τ_1 is given by

$$\tau_1=\left(\frac{f_0+f_0^{-1}K^+_{1c}/K_{1c}}{F_1+f_0^{-1}(K^+_{1c}/K_{1c})F_2}\right)^{1/2}\left(\frac{T_c-T}{T_c}\right)^{1/2}, \qquad (43)$$

where Eq. (39) has been used several times. This has the usual temperature dependence $(T_c-T)^{1/2}$ of a second-order phase transition in mean-field theory. To lowest order in τ_1, $\mu_1=f_0\tau_1$ [Eq. (40)].

In the limit of perfect nematic and smectic order used in Appendix C, $f_0=1$, $K^+_{1c}/K_{1c}=2e-1$, $F_2=F_1=2C_2(K_{1c})/I_0$, and (43) gives

$$\mu_1=(1/F_1^{1/2})(\Delta K/K_{1c})^{1/2}=[I_0\Delta K/2K_{1c}C_2(K_{1c})]^{1/2},$$

which agrees with Eq. (C12) (since $\bar{\mu}_1=e\mu_1=\mu_1/K_{1c}$).

The critical temperature (or K_{1c}) and the proportionality constant in Eq. (43) are given by Appendix C in the limit of perfect smectic-A order. To end this section we give estimates of these quantities for more realistic imperfect smectic-*A* order.

Let us assume $\eta\sim 0.8$, $\sigma\sim 0.6$ (which corresponds to $\beta V_0\sim 5$ in Fig. 4 of Ref. 3) and $\sigma_0\sim\sigma/\eta\sim 0.7$. In view of Eqs. (2) and (21), and $V_1<V_0$, it follows that

$$e'=1+O(10^{-2})\simeq 1 \qquad (44)$$

[e' is defined after Eq. (36)]. Therefore

$$s\simeq a_{20}+a_{02}=a_{20}(1+a_{02}/a_{20}), \qquad (45)$$

$$a_{02}/a_{20}\gtrsim\langle\sigma_0^2\rangle_0. \qquad (46)$$

Also

$$d\simeq a_{20}^2(\langle\sigma_0^2\rangle_0-\sigma_0^2). \qquad (47)$$

To estimate $\langle\sigma_0^2\rangle_0$ the probability distribution $e^{2\sigma_0(\zeta)}$ has been used; this gives $\sigma_0\simeq 0.66$, $\langle\sigma_0^2\rangle\simeq 0.65$. Combining these values with Eqs. (44)–(47) one obtains

$$4e'd/s^2\simeq 4\times 0.22/(1.65)^2\simeq\tfrac{1}{3}$$

and, expanding Eq. (38),

$$K_{1c}\simeq 1/s\simeq 1/1.65a_{20}. \qquad (48)$$

The average a_{20} is

$$a_{20}=\langle\mu_1^2\rangle_0\simeq\tfrac{1}{4}(\langle\cos^4\theta\rangle_0+\langle\cos^2\theta\rangle_0) \qquad (49)$$

[since $\mu_1(\Omega_1)=R_{32}(1)=\hat{z}\cdot\vec{\nu}^3(1)\vec{\nu}^2(1)\cdot\hat{y}=\cos\theta(\cos\theta\times\sin\phi\cos\psi+\cos\phi\sin\psi)$, in terms of Euler angles θ,φ,ψ]. The formula

$$\langle\sin^{2n}\theta\rangle_0\simeq\left(\frac{-\partial}{\partial A}\right)^n\ln\int_0^\infty d\theta\,\theta^{2n}e^{-A\theta^2}=\frac{n!}{A^n},$$

valid for large $A=\tfrac{1}{2}3\beta V_0\eta$, can be used to get an approximate value for $\langle\cos^4\theta\rangle_0$. With $A\simeq 7.5$ (which gives $\eta\sim 0.8$), one finds $a_{20}\simeq 0.4$ and

$$K_{1c}\simeq 1.5. \qquad (50)$$

As one expects, the range of stability of the smectic-*C* phase is decreased when the smectic-*A* order is imperfect.

Substituting $K_{1c}\simeq 1/s$ into Eq. (39) gives

$$f_0\simeq(s-a_{02})/a_{11}\simeq a_{20}/a_{11}\sim 1/\sigma_0\sim 1.4, \qquad (51)$$

which is the same as an estimate directly from the definition of f_0, $f_0=\mu_1/\tau_1\sim 1/\sigma_0$.

Similarly one obtains the order of magnitudes

$$\gamma\sim 10^{-1},\quad D_{m,n}\sim\gamma^2\beta C_1\langle\sin^2\theta\rangle_0\sim 10^{-2}\quad(m+n\geqslant 2)$$

(of course, $D_{00}=0$ by the definitions of C_1,γ,D), and

$$F_1\sim 1.$$

$|F_2|$ is significantly smaller than F_1 since, owing to Eq. (51), there is more cancellation of negative and positive contributions in F_2.

As a final check, one may easily verify that for $K_1>K_{1c}$ the free energy (27) is smaller for τ_1 (and μ_1,χ) nonvanishing than for $\tau_1=\mu_1=\chi=0$.

Of course, the calculation presented in this paper has only qualitative or semiquantitative validity. Mean-field theory has been used to describe a second-order phase transition, only the lowest Fourier component of the smectic planar structure has been included (Sec. III), and a particular simple form for the zig-zag interaction has been used (Sec. II).

VI. COMMENTS

It has been shown in this paper that steric effects, in particular the zig-zag gross shape of the molecules of a smectic material, may be able to account for the second-order smectic-*A*–smectic-*C* phase transition. From the end of Sec. V it follows that $V_1/V_0=K_1/K_0\sim 1.5/5\sim 0.3$. This estimate for the magnitude of the zig-zag interaction is small enough to be plausible (e.g., if V_0 corresponds to a nematic transition temperature of 500 °K, then a substance whose nematic interaction strength equals $V_1=0.3V_0$ has a nematic temperature of 150 °K; i.e., in effect it would show no mesophase properties).

We mentioned in Sec. I that there is some similarity between the angles χ in the smectic-*C* phase and qa in cholesteric liquid crystals. However, there are some important differences too. While χ can become as large as 45°, qa is always of the order of 1° or less. Further, qa is determined essentially by the nematic order parameter of the liquid crystal,[5] while χ is determined entirely by a biaxial order parameter (τ_1 in our model). Thus in the smectic-*C* phase the biaxial order parameters play a primary role and in the cholesteric phase only a secondary role (in the cholesteric phase the biaxialities are a consequence of the helical structure, not its cause). It is for this reason that the biaxialities in cholesteric liquid crystals are determined to be of order $(qa)^2$ and therefore small,[5,7] while in the smectic-C phase there is no such limitation on the biaxialities. From Sec. V it follows that the biaxial order parameters in the smectic-C phase may easily grow to values of $O(10^{-1})$ [e.g., put $T_c \sim 500$ °K and $T_c - T \sim 25$ °K in Eq. (43), etc.].

In view of the quite respectable values of the biaxialities predicted for the smectic-C phase it should be feasible to test the model by direct experimental observation of the biaxial anisotropy, something that is much harder to do for the cholesteric phase. Magnetic-resonance experiments can be done and perhaps also optical experiments—e.g., an optical-reflectance experiment[14] in a twisted smectic-C material.[15]

In some liquid crystals there is a direct transition from the nematic phase to the smectic-C phase with a large and apparently temperature-independent tilt angle. It is clear that in the model presented here such a direct transition would happen for sufficiently large V_1/V_0.

It may be noted that the form of our zig-zag interaction, Eq. (4b), implies that the tilt angle χ can never exceed $\frac{1}{4}\pi$. Experimentally, the rule $\chi < \frac{1}{4}\pi$ seems always to be satisfied.

The present model suggests that the natural order parameters for the smectic-C phase are $\langle \vec{R} \rangle$ and $\langle \vec{R} \cos 2\pi\zeta/d \rangle$, rather than the vector order parameters used by de Gennes[6] and McMillan.[1] It is easy to see, however, that in the limit of perfect nematic order McMillan's order parameter is essentially the same as $\langle \vec{R} \rangle$ and de Gennes's is equivalent to $\gamma \langle \vec{R} \cos 2\pi\zeta/d \rangle$, owing to Eqs. (25) and (29). (Recall $\vec{R} = \vec{\nu}^3 \vec{\nu}^2$.)

To further investigate the validity of the steric model, studies of similar compounds having a smectic phase and differing in their end chains would be useful.

The magnetic-resonance spectra of solute molecules in nematic solvents have been used to deduce information concerning the structure of the solute molecules.[16] It may be possible to gain more information, provided accurate enough measurements can be made, by using liquid-crystal solvents with biaxial orientational order.

APPENDIX A

Consider a material in the smectic-A phase and described by the effective Hamiltonian H_n of Eq. (4a). Let the axis Z be the nematic axis normal to the smectic planes (see Fig. 2). Now we imagine a uniform shearing deformation of the fluid, with the Y axis perpendicular to the shearing planes. Only the centers of mass of the molecules are shifted according to the rule $(x, y, z) \to (x, y, z + y \tan\chi)$, the nematic axis and the volume of the system remaining fixed. The resulting configuration is that of a smectic-C with tilt angle χ. The average distance between neighboring molecules in the same smectic plane has increased from w, say, to $w/\cos\chi \sim w(1+\chi^2/2)$, and this results in an increase of $\langle H_n \rangle$ proportional to χ^2 (small χ). The calculation of this increase in mean-field approximation is outlined below.

The single-molecule distribution function in the deformed state is $\rho(\theta, z - y\tan\chi)$, where $\rho(\theta, z)$ is the distribution in the original smectic-A configuration. $\rho(\theta, z)$ is periodic in z, with the period d equal to the thickness of a smectic-A layer; θ is the angle between the Z axis and the axis $\vec{\nu}^3$ of the molecule. The interaction energy of molecule 1 with the rest of the fluid is (with $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$ and $\zeta \equiv z - y\tan\chi$)

$$U_n(\chi;\, \theta_1, \zeta_1) = -\frac{V_0}{\pi^{3/2} r_0^3 \rho} \int d^3 r_2\, e^{-r^2/r_0^2} \times \int d\Omega_2 \left(\tfrac{3}{2}\cos^2\theta_{12} - \tfrac{1}{2}\right)\rho(\theta_2, \zeta_2)$$

[see Eqs. (4a) and (4c)]. Let x', y', z' denote the system of coordinates obtained by rotating the axes Z, Y about X through the angle χ,

$$x' = x,\; y' = z\sin\chi + y\cos\chi, \quad z' = z\cos\chi - y\sin\chi\,.$$

The axis Z' is normal to the new smectic planes (Fig. 2). Introducing the primed coordinates in the integral above one gets, for $\vec{r}_1$ far (on the scale of r_0) from the system's surface,

$$U_n = -\frac{V_0}{\pi^{1/2} r_0 \rho} \int_{-\infty}^{\infty} dz_2'\, e^{-z'^2_2/r_0^2} \times \int d\Omega_2 \left(\tfrac{3}{2}\cos^2\theta_{12} - \tfrac{1}{2}\right)\rho\!\left(\theta_2, \frac{z_2'}{\cos\chi}\right).$$

Changing the integration variable to $\zeta_2 = z_2'/\cos\chi$ and making the truncated Fourier expansion

$$e^{-\zeta^2/r'^2_0} = (\pi^{1/2} r_0'/L)(1 + \alpha_0' \cos 2\pi\zeta/d + \ldots),$$

$$r_0' = r_0/\cos\chi, \quad \alpha_0' = 2e^{-(\pi r_0'/d)^2},$$

in $-\frac{1}{2}L < \zeta < \frac{1}{2}L$, $L \gg r_0$, one obtains [with $\rho(\theta, \zeta) = \rho h(\theta, \zeta)$]

$$\frac{U_n}{-V_0} \simeq \frac{1}{L}\int_{-L/2}^{L/2} d\zeta_2 \int d\Omega_2 \left(1 + \alpha_0' \cos\frac{2\pi\zeta}{d}\right) \tfrac{3}{2}Q_{33}(2) h(\theta_2, \zeta_2) \tfrac{3}{2}Q_{33}(1) \simeq \tfrac{3}{2}Q_{33}(1)\left\{\eta + \cos\frac{2\pi\zeta_1}{d}\,\alpha_0\sigma\left[1 - \left(\frac{\pi r_0}{d}\right)^2 \chi^2\right]\right\};$$

η and σ are defined in Sec. III, $\overset{\leftrightarrow}{Q}(1)$ in Sec. II. [The origin of coordinates is chosen so that $h(\theta;\zeta)=h(\theta;-\zeta)$; hence $\langle \frac{3}{2}Q_{33}(2)\sin 2\pi\zeta_2/d\rangle=0$.] Thus, for small χ,

$$U_n(\chi;\theta_1,\zeta_1)=U_n(\theta_1;\zeta_1)+(\tfrac{3}{2})Q_{33}(1)\cos(2\pi\zeta_1/d)\,\overline{V}_0\sigma\chi^2\,,$$

where

$$U_n(\theta_1,\zeta_1)=-(\tfrac{3}{2})Q_{33}(1)[\eta+\cos(2\pi\zeta_1/d)\,\alpha_0\sigma]\,V_0$$

is the McMillan mean field and $\overline{V}_0=V_0\overline{\alpha}_0$ (see Sec. III). The increment in $\langle H_n\rangle$ is given by

$$(2/N)(\langle H_n\rangle_\chi-\langle H_n\rangle_0)=\langle U_n(\chi)\rangle-\langle U_n\rangle=\overline{V}_0\sigma^2\chi^2.$$

APPENDIX B

Let a system with single-particle coordinates τ be described by a mean field $U(\tau;\psi)$ of the form

$$U(\tau;\psi)=-\sum\mu_nV_n(\tau)\psi^n\quad(n=0,1,2,\ldots)\,.$$

The μ_n are order parameters given by

$$\mu_{n'}=\langle V_n(\tau)\rangle\,,\tag{B1}$$

where

$$\langle f(\tau)\rangle\equiv\frac{1}{Z_1}\int d\tau\,e^{-\beta U}f(\tau)\,,$$

$$Z_1=\int d\tau\,e^{-\beta U}\,.$$

(n' may be different from n; however, such unsymmetric terms in U always occur in pairs, $\langle V_{n'}\rangle V_n+\langle V_n\rangle V_{n'}$.) The parameter ψ can be an external field, but it can also be an internal parameter describing geometric relations between different parts of the system. An example of this latter case, other than the smectic-*C* mesophase considered in this paper, is provided by cholesteric liquid crystals where $\psi=q=$ pitch wave number.

In the case that ψ is an internal parameter, its value in equilibrium minimizes the appropriate free energy. We now show that in the mean-field approximation this condition reduces to minimization of the energy with respect to the explicit ψ; i.e., ψ satisfies

$$\frac{\partial\langle U\rangle}{\partial\psi}=0\,,\tag{B2}$$

where $\langle U\rangle=-\sum\mu_n\mu_{n'}\psi^n$ and the μ_n, ψ are considered independent.

The mean-field expression for the entropy (per molecule) is

$$TS_1=U_1-F_1=-\sum\mu_n\mu_{n'}\psi^n+\beta^{-1}\ln Z_1$$

(the subscript 1 is used to indicate single-particle quantities for a molecule in the mean field). We have

$$\frac{T\partial S_1}{\partial\psi}=-\sum n\mu_n\mu_{n'}\psi^{n-1}+\frac{\beta^{-1}}{Z_1}\frac{\partial Z_1}{\partial\psi}$$

$$=-\sum n\mu_n(\mu_{n'}-\langle V_n(\tau)\rangle)\psi^{n-1}=0\tag{B3}$$

in view of (B1). The free energy is

$$F=\tfrac{1}{2}\langle U\rangle-TS_1\,.\tag{B4}$$

Since $\partial F/\partial\mu_n=0$ [equivalent to (B1)], it follows that $dF/d\psi=\partial F/\partial\psi$ and, by (B4) and (B3), that Eq. (B2) is satisfied in equilibrium.

The mean field given by Eq. (26) in the text is of the more general form $U(\tau;\psi)=\sum\mu_{n,m}\times V_{n,m}(\tau)\psi^n$, where some of the $V_{n,m}(\tau)$ (and the corresponding order parameters $\mu_{n',m'}$) may be the same for different n, m. It is easy to see, however, that the above argument still holds.

APPENDIX C

We consider here the limiting case of perfect nematic and smectic order, i.e.,

$$\eta\to1,\quad\sigma_0,\sigma\to1\,.\tag{C1}$$

Two reasons make it worthwhile to study this case: (a) It provides a simple and transparent example of our model for the smectic-*C* phase; (b) in this simple case it is easy to see that there is no first-order phase transition competing with the second-order transition obtained in Sec. V.

In the limit (C1)

$$\tau_1(\Omega,\zeta)=\mu_1(\Omega)\sigma_0(\zeta)\sim\mu_1(\Omega)\,,\quad\tau_1\approx\mu_1\sigma_0\sim\mu_1\,,$$

and the mean field, Eq. (26), can be written

$$U\sim U_0+\chi^2U_a-2\mu_1(\Omega)(\mu_1+\chi\overline{V}_2/2V_1)V_1-\mu_1\chi\overline{V}_2\,.\tag{C2}$$

Further, in the limit (C1), with $\epsilon_1=\hat{z}\cdot\vec{\nu}^3(1)=\pm1$,

$$\mu_1(\Omega_1)=R_{32}(1)\approx\epsilon_1\vec{\nu}^2(1)\cdot\hat{y}\equiv\epsilon_1\cos\psi_1\,.$$

Hence the free energy per particle, F, is given in the mean-field approximation (see Appendix B) by

$$\beta F=\tfrac{1}{2}(-\beta\langle U_0\rangle-\chi^2\beta C_1+2\mu_1\overline{\mu}_1K_1+\mu_1\chi\overline{K}_2)-\ln Z_1\,,\tag{C3}$$

where

$$Z_1\simeq Z_1^0e^{-\beta C_1\chi^2+\mu_1\overline{K}_2\chi}\int_{-\pi}^{\pi}d\psi\,e^{2K_1\overline{\mu}_1\cos\psi}\,,\tag{C4}$$

$$\overline{\mu}_1=\mu_1+\chi\overline{V}_2/2V_1\,,\tag{C5}$$

and $K_1,\overline{K}_2$ are defined in Sec. V. The fact that the fluctuations of U_a away from its average value C_1 are negligible in the limit (C1) has been used in Eq. (C4).

From (C3) and (C4) one can see that the operation $\mu_1\to-\mu_1$, $\chi\to-\chi$ is a symmetry of the system;

physically, it corresponds to rotating the system by 180° about the Z axis (Fig. 2). It follows that we can restrict ourselves to

$$0 \leqslant \mu_1 \leqslant 1, \quad \chi \geqslant 0 \tag{C6}$$

[χ has the same sign as μ_1, Eq. (C8)].

It is easy to see that the equilibrium conditions $\partial F/\partial\mu_1 = \partial F/\partial\chi = 0$ lead to

$$\mu_1 - \langle \cos\psi \rangle = 0\,, \tag{C7}$$

$$\chi = (\overline{V}_2/C_1)\langle \cos\psi \rangle\,, \tag{C8}$$

where the average reduces to

$$\langle \cos\psi \rangle = \frac{1}{Z_1'} \int \cos\psi\, e^{2K_1\overline{\mu}_1 \cos\psi}\, d\psi\,,$$

$$Z_1' = \int e^{2K_1\overline{\mu}_1 \cos\psi}\, d\psi\,.$$

We show now that the conditions (C7) and (C8) have just *one* solution in the interval given by (C6); as the temperature is lowered, or K_1 increased, the solution goes continuously from $\mu_1 = \chi = 0$ to μ_1, $\chi > 0$, at a critical value K_{1C}.

Substituting (C7) in (C8) gives

$$\chi = (\overline{V}_2/C_1)\mu_1\,. \tag{C9}$$

Equation (C7) can be written

$$0 = \mu_1 Z_1' - \sum_{n=0}^{\infty} (2K_1\overline{\mu}_1)^{2n+1} \frac{I_{2n+2}}{(2n+1)!}\,,$$

or, on using (C9),

$$0 = \sum_{0}^{\infty} (2K_1\overline{\mu}_1)^{2n} \frac{C_{2n}}{(2n)!}\,, \tag{C10}$$

where

$$C_{2n}(K_1) = I_{2n} - (2K_1 e/2n+1) I_{2n+2}\,,$$

$$e = 1 + \overline{V}_2^2/2V_1C_1\,,$$

$$I_{2n} = \int_0^{2\pi} \cos^{2n}\psi\, d\psi\,.$$

Since $I_{2n} > I_{2n+2}$, $C_{2n} > 0$ for all n if K_1 is small, e.g., $K_1 < (2e)^{-1}$; then the right-hand side of (C10) is positive for $\overline{\mu}_1 = e\mu_1 > 0$, and the only solution is $\mu_1 = 0$; i.e., at high temperatures the unique solution of Eqs. (C7) and (C8) is $\mu_1 = \chi_1 = 0$. At

$$K_{1c} = I_0/2eI_2 = 1/e \tag{C11}$$

C_0 becomes zero, and for $K_1 > K_{1c}$, $C_0 < 0$. For small $K_1 - K_{1c}$, $C_{2n} > 0$, for $n \geqslant 1$, and it follows that there is just one solution $\overline{\mu}_1$ of Eq. (C10) [since $-|C_0| + \sum_1^\infty (2K_1\overline{\mu}_1)^{2n} C_{2n}/(2n)!$, with $C_{2n} > 0$, is an increasing function of $\overline{\mu}_1$ for $\overline{\mu}_1 > 0$].

For small $\Delta K = K_1 - K_{1c}$, Eq. (C10) gives

$$\begin{aligned} 0 &= C_0(K_1) + \tfrac{1}{2}(2K_1\overline{\mu}_1)^2 C_2(K_1) + \cdots \\ &\simeq -2eI_2\Delta K + \tfrac{1}{2}(2K_{1c}\overline{\mu}_1)^2 C_2(K_{1c})\,, \end{aligned}$$

so that

$$\overline{\mu}_1 \simeq \frac{[I_0 \Delta K/2K_{1c} C_2(K_{1c})]^{1/2}}{K_{1c}} \sim \left(\frac{T - T_c}{T_c}\right)^{1/2}\,,$$

with $K_{1c} = \beta_c V_1 = V_1/k_B T_c$. Note $K_{1c} \lesssim 1$ in the present case.

Note added in proof. We have not been very explicit above about how the nematic axis Z is defined. An appropriate general definition is that the Z axis is the principal axis of $\langle \vec{Q} \rangle$ corresponding to the largest eigenvalue $2\eta/3$. It may be noted also that in general $\langle \vec{Q} \rangle$ can be biaxial, $\langle \vec{Q} \rangle = \eta(\hat{z}\hat{z} - \frac{1}{3}) + \Delta(\hat{x}\hat{x} - \hat{y}\hat{y})$ (Priest and Lubensky, Ref. 2; Ref. 7). The possibility $\Delta \neq 0$ was disregarded in Appendix A, but it is easy to see that to $O(\chi^2)$ in the free energy no error was introduced. This is because the biaxiality Δ is unchanged by a 180° rotation of the system about the Z axis, which means that Δ is an even function of μ_1, τ_1, χ, i.e., $\Delta = O(\chi^2)$. Therefore, the additional terms in the mean field of Appendix A, which are of order $(Q_{11} - Q_{22})\Delta$, make contributions only of order $\Delta^2 \sim \chi^4$ to the increment $\langle H_n \rangle_\chi - \langle H_n \rangle$ and the free energy.

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[10] This is discussed in some detail in the article by

A. Wulf and A. G. De Rocco [J. Chem. Phys. 55, 12 (1971)], where some further references may be found.

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