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Simple Molecular Theory of the Smectic *C* Phase*

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A physical picture of the smectic *C* phase is proposed in which the molecules rotate freely about their long axes in the smectic *A* phase and this rotation is frozen out in the smectic *C* phase. This picture is in contrast with the accepted view that the long axis of the molecules is normal to the smectic planes in the smectic *A* phase and tilted in the smectic *C* phase. A microscopic theory of this phase transition is constructed using the dipole-dipole interaction of the permanent molecular dipole moments. Three ordered phases are found, one with the physical properties of the smectic *C* phase (tilted director, optically biaxial, second-order smectic-*A* –smectic-*C* phase transition). The second-ordered phase is a two-dimensional ferroelectric and the third, low-temperature ordered phase is both tilted and ferroelectric.

I. INTRODUCTION

The nature of the molecular order in the nematic and smectic *A* phases has been clear for some time. In the nematic phase the long molecular axes lie parallel to an axis in space and in the smectic *A* phase the long axes are parallel and the molecular centers sit on parallel equidistant planes. The long axes are perpendicular to the planes. Given the nature of the molecular order one can write down theories of various sorts and the theoretical situation is well advanced in these two phases. In the nematic phase one has a microscopic[1] theory, a continuum theory,[2,3] a Landau theory,[4] and a hydrodynamic theory.[5-7] In the smectic *A* phase one has a microscopic theory[8,9] and a Landau theory.[10,11]

The accepted picture of the smectic *C* phase is that the molecular long axis tilts over with respect to the plane normal and deGennes[12] has constructed a Landau theory using the tilt angle as an order parameter. In this paper I wish to present an alternative physical picture of the smectic *C* phase in which the tilt angle plays only a secondary role. The primary role is played by molecular rotation around the long axis; this rotation is assumed to be free in the smectic *A* phase and frozen out in the smectic *C* phase. Liquid-crystal molecules usually have two or three large permanent electric dipole moments associated with oxygen and nitrogen atoms in their structure. We investigate here a simple molecular model with dipole-dipole interactions and show that one of the ordered phases of this model has the physical properties of the smectic *C* phase.

We adopt a model in which the smectic *A* order is well established and the molecules are parallel and sit on planes. The remaining molecular motions which are permitted are rotation about the long axis and translation in one plane. We assume that there are permanent dipole moments attached to the molecules and examine the rotational phase transitions within the mean-field approximation. The model is quasi-two-dimensional in that the intraplanar interactions between molecules are far stronger than the interplanar interactions. In the calculations which follow we will usually neglect the interplanar interactions and treat a two-dimensional model of motion of the molecules in one smectic plane; corrections due to interplanar interactions are inserted at the end of each calculation.

The dipole model which we treat is surprisingly rich and exhibits three ordered (smectic-*C*-like) phases in addition to the disordered (in one plane) smectic *A* phase. The phase transitions between these phases are all second order and one of the ordered phases has the physical properties of the smectic *C* phase. Each of the three ordered phases is optically biaxial. The other physical properties are as follows.

(i) *Smectic C*. When the molecular structure is dominated by two outboard oppositely directed dipoles the first ordered phase is shown in Fig. 1(a). The outboard dipoles on one side of the plane are oriented parallel and the central dipoles (if any) are randomly oriented. The long molecular axis tilts over in the direction of polarization with the tilt angle proportional to $(T_c - T)^{1/2}$. The smectic *A* phase is optically uniaxial and the optical properties are continuous through the phase transition. The optical anisotropy in the smectic plane is proportional to $T_c - T$. These are the known physical properties of the smectic *C* phase.

(ii) *Smectic* C_1. When the molecular structure is dominated by one central dipole the first ordered phase is a two-dimensional ferroelectric [Fig. 1(b)]. The central dipoles are parallel to each other and the outboard dipoles are randomly oriented. Whether or not the three-dimensional structure is ferroelectric or antiferroelectric depends on the sign of the interplanar interaction. The transverse dielectric constant exhibits a Curie-Weiss singularity $(T-T_1)^{-1}$ near the phase transition and there is no tilt of the molecular axes.

(iii) *Smectic* C_2. If the central and outboard dipole moments are comparable in magnitude there exists a low-temperature ordered phase below either smectic *C* or smectic C_1. In this phase [Fig. 1(c)] both the central and outboard dipole moments are aligned and this phase is both tilted and a two-dimensional ferroelectric.

The plan of the paper is as follows. In Sec. II we will define the model and solve the self-consistent field equations to find the order parameters and transition temperatures. In Sec. III we will calculate the physical properties of the three ordered phases. In Sec. IV we will derive a Landau theory (an elastic theory) from the microscopic theory for the smectic *C* phase. In Sec. V we will compare the smectic *C* model with the available experiments and in Sec. VI we discuss the relationship between the molecular structure and the stability of the smectic *C* phase.

II. THEORETICAL MODEL

Consider one plane of a smectic liquid crystal and call it the x-y plane. The long rodlike molecules have their centers on the plane and move as a two-dimensional liquid in the plane. Their long axes are parallel to the z axis. We assume that there are three electric dipole moments rigidly attached to the molecule on its central axis and directed perpendicular to that axis. One dipole of magnitude μ_1 is at the molecular center and its direction defines the short axis of the molecule. A second dipole of magnitude μ_2 sits a distance $d/2$ above the first and parallel to it. A third dipole of magnitude μ_2 sits a distance $d/2$ below the first and antiparallel to it [Fig. 1(d)]. The dipole-dipole interaction is

$$U=\sum_{i<j}\frac{\vec{\mu}_i\cdot\vec{\mu}_j}{\epsilon_\infty r_{ij}^3}-\frac{3\vec{\mu}_i\cdot\vec{r}_{ij}\,\vec{\mu}_j\cdot\vec{r}_{ij}}{\epsilon_\infty r_{ij}^5}, \tag{1}$$

where r_{ij} is the distance between dipoles and ϵ_∞ is the high-frequency dielectric constant of the medium. This, together with the intermolecular correlation function, defines the model.

We will calculate the properties of the model using the self-consistent-field method by calculating the average electric field at each dipole due to the other dipoles. The molecules are free to rotate around the long axis, to turn upside down, and to translate in the x-y plane. Take φ_i as the angle between the central dipole of the ith molecule and the x axis. Call the configuration with the central dipole parallel to the upper dipole the (+) configuration and that with the central dipole parallel to the lower dipole the (−) configuration. We specify a single-particle angular distribution function for a molecule by writing down a single-particle potential for both configurations:

$$V_+(\varphi)=-v_+\cos(\varphi), \tag{2}$$

$$V_-(\varphi)=-v_-\cos(\varphi). \tag{3}$$

The distribution function is then

$$f_+(\varphi)=(1/N)e^{(v_+\cos\varphi/kT)}, \tag{4}$$

$$f_-(\varphi)=(1/N)e^{(v_-\cos\varphi/kT)}, \tag{5}$$

$$N=\int_0^{2\pi}d\varphi\,[e^{v_+\cos\varphi/kT}+e^{v_-\cos\varphi/kT}]. \tag{6}$$

With this distribution function the average central dipole moment is

$$\mu_1\alpha=\mu_1\int_0^{2\pi}d\varphi\cos\varphi[f_+(\varphi)+f_-(\varphi)] \tag{7}$$

and the average upper dipole moment is

$$\mu_2\beta=\mu_2\int_0^{2\pi}d\varphi\cos\varphi[f_+(\varphi)-f_-(\varphi)]. \tag{8}$$

If the spacing between dipoles on one molecule, d, is somewhat larger than the intermolecular spacing we can neglect the interactions between

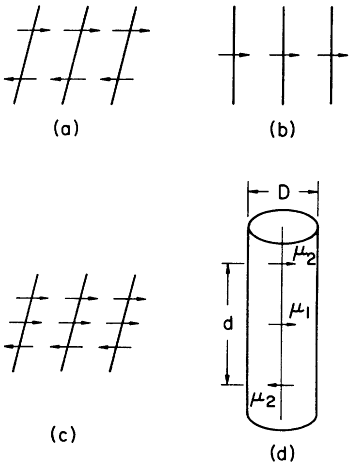

FIG. 1. (a) Molecular order in the smectic *C* phase with the outboard dipoles aligned (central dipoles random). (b) Molecular order in the smectic C_1 phase with the central dipoles aligned (outboard dipoles random). (c) Molecular model in the smectic C_2 phase with all dipoles aligned. (d) Molecular model: a cylindrical shape with length *L* and width *D* and three electric dipoles rigidly attached to the central axis, one dipole of magnitude μ_1 at the molecular center and two dipoles of magnitude μ_2 at a distance $d/2$ from the center.

dipoles on different levels. Then the electric field at the central dipole of one molecule is determined by the average central dipole moment of the other molecules and by the planar intermolecular correlation function $g_2(r)$:

$$E_1 = \frac{\pi\mu_1\alpha}{\epsilon_\infty}\int_0^\infty \frac{r\,dr\,g_2(r)}{r^3}\,. \tag{9}$$

We take a simple approximation for the correlation function,

$$g_2(r) = \begin{cases} 0\,, & r<D \\ n_2, & r>D \end{cases} \tag{10}$$

$$\pi D^2 n_2 = 1,$$

where n_2 is the number of molecules' per unit area. Then

$$E_1 = \frac{\mu_1\alpha(\pi n_2)^{3/2}}{\epsilon_\infty}\,. \tag{11}$$

Similarly the electric field on the upper (and lower) dipole is

$$E_2 = \frac{\mu_2\beta(\pi n_2)^{3/2}}{\epsilon_\infty}. \tag{12}$$

Then the average potential on the molecule in the (+) configuration is

$$\overline{V}_+(\varphi) = -(\mu_1 E_1 + 2\mu_2 E_2)\cos\varphi\,, \tag{13}$$

and in the (−) configuration

$$\overline{V}_-(\varphi) = -(\mu_1 E_1 - 2\mu_2 E_2)\cos\varphi\,. \tag{14}$$

Self-consistency requires that these average potentials be equal to the starting potentials (2) and (3) so that

$$v_+ = \frac{(\pi n_2)^{3/2}}{\epsilon_\infty}(\mu_1^2\alpha + 2\mu_2^2\beta)\,, \tag{15}$$

$$v_- = \frac{(\pi n_2)^{3/2}}{\epsilon_\infty}(\mu_1^2\alpha - 2\mu_2^2\beta)\,. \tag{16}$$

Near the phase transition the order parameters will be small and we can evaluate the integrals (7) and (8) by expanding the exponentials in a power series. We find

$$N = 4\pi\{1 + \tfrac{1}{8}[(v_+/kT)^2 + (v_-/kT)^2] + \cdots\}\,, \tag{17}$$

$$\alpha = \frac{\pi}{N}\{(v_+/kT) + (v_-/kT) + \tfrac{1}{8}[(v_+/kT)^3 + (v_-/kT)^3] + \cdots\}\,, \tag{18}$$

$$\beta = \frac{\pi}{N}\{(v_+/kT) - (v_-/kT) + \tfrac{1}{8}[(v_+/kT)^3 - (v_-/kT)^3] + \cdots\}\,. \tag{19}$$

Writing

$$A = \frac{(\pi n_2)^{3/2}\mu_1^2\alpha}{\epsilon_\infty kT}\,, \tag{20}$$

$$B = \frac{(\pi n_2)^{3/2}\mu_2^2 2\beta}{\epsilon_\infty kT}\,, \tag{21}$$

and substituting (15) and (16) into (17)–(19) we find

$$\frac{\epsilon_\infty kT}{(\pi n_2)^{3/2}\mu_1^2}A = \tfrac{1}{2}A - \tfrac{1}{16}A^3 + \tfrac{1}{16}AB^2\,, \tag{22}$$

$$\frac{\epsilon_\infty kT}{(\pi n_2)^{3/2}2\mu_2^2}B = \tfrac{1}{2}B - \tfrac{1}{16}B^3 + \tfrac{1}{16}BA^2\,. \tag{23}$$

When $\mu_1^2 > 2\mu_2^2$ we find a phase transition at

$$T_1 = \frac{\mu_1^2(\pi n_2)^{3/2}}{2k\epsilon_\infty}\,, \tag{24}$$

with

$$A = [8(1 - T/T_1)]^{1/2} \tag{25}$$

or

$$\alpha = [2(1 - T/T_1)]^{1/2}\,, \tag{26}$$

and $B = \beta = 0$.

We name the phase with $\alpha \neq 0$, $\beta = 0$ the smectic C_1 phase. Smectic *A* in this model has $\alpha = \beta = 0$.

The phase transition is second order and the ordered phase has a net polarization in the plane (two-dimensional ferroelectric). Substituting (25) into (23) we find a second phase transition at

$$T_2 = \frac{2T_1 T_c}{T_1 + T_c}\,, \tag{27}$$

where

$$T_c = \frac{\mu_2^2(\pi n_2)^{3/2}}{k\epsilon_\infty}\,, \tag{28}$$

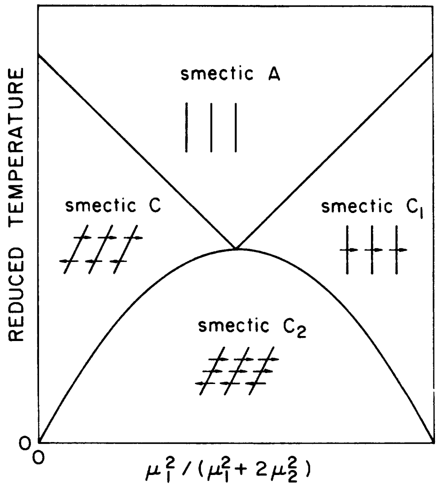

FIG. 2. Phase diagram of the theoretical model showing the transition temperatures in reduced units $\{2\epsilon_\infty kT/[(\mu_1^2+2\mu_2^2)(\pi n_2)^{3/2}]\}$ versus the relative magnitude of the central dipole moment.

and

$$B=4[(1-T/T_2)]^{1/2} \tag{29}$$

or

$$\beta=\frac{4T_1}{T_1+T_c}[(1-T/T_2)]^{1/2}. \tag{30}$$

We name the phase with $\alpha \neq 0$, $\beta \neq 0$ the smectic C_2 phase. The smectic-C_1–smectic-C_2 phase transition is second order.

If instead we have $2\mu_2^2 > \mu_1^2$ we have a phase transition at T_c with

$$\beta=[2(1-T/T_c)]^{1/2}, \tag{31}$$

which we label smectic $C(\alpha=0,\ \beta\neq 0)$, and a second phase transition at T_2 into the smectic C_2 phase. Both phase transitions are second order. The calculated phase diagram is given in Fig. 2.

III. PHYSICAL PROPERTIES

A. Optical Properties

We assume that the molecules are optically anisotropic in the x-y plane and that the molecular polarizability is of the form

$$p(\varphi_1)=p_0+p_1(\cos^2\varphi_1-\tfrac{1}{2}), \tag{32}$$

where φ_1 is the angle between the measuring field and the central dipole axis. Averaging (32) over the distribution function leads to

$$\bar{p}(\varphi_2)=p_0+\tfrac{1}{8}p_1[(T_1/T)^2\alpha^2+(T_c/T)^2\beta^2] \times(\cos^2\varphi_2-\tfrac{1}{2}), \tag{33}$$

where φ_2 is the angle between the measuring field and the x axis (the preferred axis). The smectic A phase is uniaxial ($\alpha=\beta=0$) and the three ordered phases are biaxial. The optical anisotropy in the plane vanishes at the phase transition and increases linearly with temperature below the transition temperature in the smectic C and smectic C_1 phases.

B. Tilt Angle

Suppose that the outboard dipoles are not perpendicular to the long axis but have a component $\mu_2\delta$ along the axis and are still antiparallel to each other. The torque to tilt it over in the x direction is $3kT_c\delta\beta$. There will be a restoring torque $-K\theta$, where θ is the tilt angle and K is an elastic constant characteristic of the smectic A phase. Equating torques we find the tilt angle

$$\theta=\frac{3kT_2\delta\beta}{K}, \tag{34}$$

which is

$$\theta=\frac{3kT_2\delta}{K}[2(1-T/T_c)]^{1/2} \tag{35}$$

in the smectic C phase and

$$\theta=\frac{3kT_2\delta}{K}\,\frac{4T_1}{T_1+T_c}[(1-T/T_2)]^{1/2} \tag{36}$$

in the smectic C_2 phase when the smectic C_1 phase lies at higher temperature. There is no tilt in the smectic C_1 phase. In the deGennes phenomenological theory the tilt angle is taken as the order parameter, whereas in the present microscropic theory the tilt angle passively follows the order parameter β.

C. Dielectric Constant

According to the model the smectic C_1 phase is an indifferent ferroelectric and one expects an anomaly in the low-frequency dielectric constant at the smectic-A–smectic-C_1 phase transition. In the smectic A phase with an external field present Eq. (22) reduces to

$$\left(\frac{T}{T_1}-1\right)A=\frac{\mu_1E_{\text{ex}}}{\epsilon_\infty kT}. \tag{37}$$

The external field is equal to the applied field E minus $4\pi P$, where P is the induced polarization

$$P=n_3\mu_1\alpha=\frac{n_3\mu_1TA}{2T_1}. \tag{38}$$

We find

$$A=\frac{\mu_1E}{\epsilon_\infty kT}\left[\frac{T}{T_1}-1+\frac{2\pi n_3\mu_1^2}{\epsilon_\infty kT_1}\right]^{-1}. \tag{39}$$

The dielectric constant ϵ is given by

$$\frac{E}{\epsilon}=\frac{E-4\pi P}{\epsilon_\infty}, \tag{40}$$

and we find

$$\epsilon=\epsilon_\infty\left[1+\frac{2\pi n_3\mu_1^2}{\epsilon_\infty k(T-T_1)}\right], \tag{41}$$

which exhibits a ferroelectric (infinite) anomaly at the phase transition. If this phase is actually antiferroelectric the dielectric constant will reach a large but finite value at the phase transition.

IV. LANDAU THEORY

In this section we will write down a Landau theory (an elastic theory) for the smectic C phase and derive Landau-theory constants from the microscopic theory. The natural order parameter for the smectic C phase is a two-dimensional real vector $\vec{\beta}(\vec{x})$, where the magnitude is equal to the local orientational order

$$|\vec{\beta}(\vec{x})|=\langle\cos\varphi\rangle \tag{42}$$

and the direction is taken to be the direction of polarization of the upper-level dipoles. This vector lies in the smectic plane. Let $\vec{p}$ be the smectic plane normal and $\vec{n}$ be the direction of the long molecular axis; the tilt angle is then $\vec{\theta}=\vec{p}\times\vec{n}$. We write down the following expression for the free energy per molecule:

$$\begin{aligned}F=&\tfrac{1}{2}A(T-T_c)|\vec{\beta}|^2+\tfrac{1}{4}B|\vec{\beta}|^4\\&+\tfrac{1}{2}C_{11}(\vec{\nabla}\cdot\vec{\beta})^2+\tfrac{1}{2}C_{33}(\vec{p}\cdot(\vec{\nabla}\times\vec{\beta}))^2\\&+\tfrac{1}{2}C_{22}|\vec{p}\times(\vec{\nabla}\times\vec{\beta})|^2-2\mu_2\vec{\beta}\cdot\vec{E}\\&+G\vec{n}\cdot\vec{\beta}+\tfrac{1}{2}K|\vec{\theta}|^2\,.\end{aligned}\tag{43}$$

The first two terms are the usual second- and fourth-order terms in the Landau theory of a second-order phase transition, and the gradient terms are analogous to the Oseen–Frank elastic energy of a nematic. The next term gives the coupling to a fictitious electric field which points in the $\vec{E}$ direction on the upper dipoles, and in the $-\vec{E}$ direction on the lower dipoles. The last two terms involving the director produce the tilt.

We will derive the terms in this expression from the microscopic theory below. The easy way to carry out that derivation is to compute the response of the order parameter $\vec{\beta}$ to an external field $\vec{E}$ according to both the Landau and microscopic theories, and to equate these responses. We first calculate the response function using the Landau theory. Suppose the smectic C is aligned in the x direction and the field is applied in the y direction. We write

$$\vec{E}=\hat{y}E_1e^{-i\vec{q}\cdot\vec{r}}\,,\tag{44}$$

$$\vec{\beta}(\vec{r})=\beta_0\hat{x}+\beta_1e^{i\vec{q}\cdot\vec{r}}\hat{y}\,,\tag{45}$$

$$\beta_0^2=A(T_c-T)/B\,.\tag{46}$$

The free energy is then

$$F(\vec{\beta})=F(\beta_0)+[\tfrac{1}{2}C_{11}q_y{}^2+\tfrac{1}{2}C_{33}q_x{}^2]\beta_1^2-2\mu_2\beta_1E_1\,.\tag{47}$$

Minimizing F with respect to β_1 we find

$$\beta_1=2\mu_2E_1/(C_{11}q_y{}^2+C_{33}q_x{}^2)\,.\tag{48}$$

Similarly, for E in the x direction, we write

$$\vec{E}=\hat{x}E_1e^{-i\vec{q}\cdot\vec{r}}\,,\tag{49}$$

$$\vec{\beta}(\vec{r})=(\beta_0+\beta_1e^{i\vec{q}\cdot\vec{r}})\hat{x}\tag{50}$$

and find

$$\beta_1=2\mu_2E_1/(2A(T_c-T)+C_{11}q_x{}^2+C_{33}q_y{}^2)\,.\tag{51}$$

We now calculate the response function according to the microscopic theory. We take a two-dipole model with one dipole of magnitude μ_2 sitting a distance $d/2$ above the molecular center and normal to the long axis and a second dipole sitting $d/2$ below the molecular center and antiparallel to the first. It turns out that we cannot neglect the interactions between the dipoles on different levels in this calculation. We assume that the smectic C is oriented in the x direction and apply an external field E_1 in the y direction. The external potential is

$$V_{\text{ex}}(\vec{r},\varphi)=-2\mu_2E_1e^{i\vec{q}\cdot\vec{r}}\sin\varphi\,,\tag{52}$$

where $\vec{r}$ is the position of a molecule and φ is the angle between the upper dipole and the x axis. We use the self-consistent-field method and assume a single-particle potential

$$V(\vec{r},\varphi)=-v_0\cos\varphi-v_q e^{i\vec{q}\cdot\vec{r}}\sin\varphi\,.\tag{53}$$

The single-particle distribution is then

$$f(\vec{r},\varphi)=e^{-V(\vec{r},\varphi)/kT}\Big/\int d^2r\,d\varphi\;e^{-V(\vec{r},\varphi)/kT}\,.\tag{54}$$

As before, one calculates the average potential which one molecule feels due to its dipole-dipole interaction with the other molecules. For self-consistency this calculated potential plus the external potential must equal the starting potential V. The self-consistency equation is

$$V(\vec{r}_1,\varphi_1)=2n_2\sum_{l=1}^{2}\int d^2r_2\,d\varphi_2 f(\vec{r}_2,\varphi_2)\times U(r_{12},\varphi_1,\varphi_2)+V_{\text{ex}}(\vec{r}_1,\varphi_1)\,,\tag{55}$$

where the sum is over the two levels and U is the dipole-dipole interaction (1). In the integral one excludes the area where $|\vec{r}_1-\vec{r}_2|<D$, the molecular diameter. The integral is tractable if in the distribution function one first expands $\exp(-v_q e^{i\vec{q}\cdot\vec{r}}\sin\varphi)$ to first order in v_q and then expands $e^{i\vec{q}\cdot\vec{r}}$ to second order in q. One finds

$$\begin{aligned}-v_0\cos\varphi_1-v_q e^{+\vec{q}\cdot\vec{r}_1}\sin\varphi_1=&\frac{-2\mu_2^2}{\epsilon_\infty}(\pi n_2)^{3/2}(1-Y^{-3})\langle\cos\varphi_2\rangle_0\cos\varphi_1\\&-\frac{2\mu_2^2(\pi n_2)^{3/2}}{\epsilon_\infty kT}\langle\sin^2\varphi_2\rangle_0 v_q e^{i\vec{q}\cdot\vec{r}_1}\sin\varphi_1\\&\times[(1-Y^{-3})-(q_xD)^2(1-Y^{-3})/8-(q_yD)^2(16Y-5-8Y^{-1}-3Y^{-3})/8]-2\mu_2E_1e^{i\vec{q}\cdot\vec{r}_1}\sin\varphi_1\,,\end{aligned}\tag{56}$$

where

$$Y=(1+d^2/D^2)^{1/2} \tag{57}$$

and

$$\langle g(\varphi)\rangle_0 \equiv \frac{\int d\varphi\, g(\varphi)e^{v_0 \cos\varphi/kT}}{\int d\varphi\, e^{v_0 \cos\varphi/kT}} . \tag{58}$$

Equating coefficients of $\cos\varphi_1$ and $\sin\varphi_1$ one finds the self-consistency equations for v_0 and v_q. Expanding the integrals in $\langle \cos\varphi_2\rangle$ near T_c one finds

$$v_0=kT[8(1-T/T_c)]^{1/2}, \tag{59}$$

$$kT_c=\mu_2^2(\pi n_2)^{3/2}(1-Y^{-3})/\epsilon_\infty . \tag{60}$$

Including the dipole-dipole interaction between levels reduces T_c by the factor $(1-Y^{-3})$. We can now calculate $\langle \sin^2\varphi_2\rangle$ and find

$$\beta_1=\frac{v_q}{2kT_c}=2\mu_2E_1\left\{kT_c\left[\frac{q_x{}^2D^2}{4}+\frac{q_y{}^2D^2}{4}\,\frac{(16Y-5-8Y^{-1}-3Y^{-3})}{(1-Y^{-3})}\right]\right\}^{-1} . \tag{61}$$

Identifying coefficients in (61) and (48) we find

$$C_{11}=kT_cD^2/4, \tag{62}$$

$$C_{33}=\frac{kT_cD^2}{4}\,\frac{(16Y-5-8Y^{-1}-3Y^{-3})}{(1-Y^{-3})} . \tag{63}$$

Both elastic constants are positive for all values of d/D. Neglecting the dipole interaction between levels is equivalent to letting $d\to\infty$ or $Y\to\infty$, which means C_{22} is infinite. Thus, this approximation is inadmissible when calculating elastic constants. With the external field in the x direction we find

$$\beta_1=2\mu_2E_1\left\{kT_c\left[4\left(1-\frac{T}{T_c}\right)+\frac{q_x{}^2D^2}{4}\,\frac{(16Y-5-8Y^{-1}-3Y^{-3})}{(1-Y^{-3})}+\frac{q_y{}^2D^2}{4}\right]\right\}^{-1} . \tag{64}$$

Comparing (64) with (51) we find

$$A=2k . \tag{65}$$

The temperature dependence of the order parameter is

$$\beta_0^2=2(T_c-T)/T_c . \tag{66}$$

Comparing (66) with (46) we find

$$B=kT_c . \tag{67}$$

If one assumes that the translational motion of molecules on different smectic planes is uncorrelated there is no electrostatic interaction between planes. We suppose that there is a weak steric interaction between molecules on neighboring planes when the ends of the molecules are touching:

$$\begin{aligned} U^1 &= -J\cos(\varphi_1-\varphi_2), \quad |\vec{r}_1-\vec{r}_2)\times\vec{p}\,|<D \\ &=0 \qquad\qquad \text{otherwise.} \end{aligned} \tag{68}$$

Then the free energy per molecule is

$$F^1=-J\sum_i\cos(\varphi_i-\varphi_j), \tag{69}$$

where φ_i is the angle of $\vec{\beta}$ in the ith plane and the sum is over neighboring planes. One finds from this expression the twist elastic constant

$$C_{22}=2Jl^2, \tag{70}$$

where l is the interplanar spacing.

From Sec. III B the torque tending to tilt over one molecule is $3kT_c\delta\beta$ so that

$$G=3kT_c\delta . \tag{71}$$

The elastic constant K is a property of the smectic A phase and cannot be calculated from the model. This completes the derivation of the Landau theory.

V. COMPARISON WITH EXPERIMENT

In this section we want to compare the predictions of the theory of the smectic C phase with experiment. The model predicts that the smectic-A–smectic-C phase transition is second order (if it is isolated in temperature from other liquid-crystal phase transitions). In a differential-scanning-calorimeter curve one usually sees a small peak at this phase transition which puts an upper limit of about $0.02R_0$ on the transition entropy. However, physical properties such as tilt angle appear to be continuous at the phase transition,[13] indicating that the phase transition is truly second order.

The model predicts a tilt angle varying as $(T_c-T)^{1/2}$. The model was solved in the classical mean-field approximation, which produces an exponent of $\frac{1}{2}$. One does not expect the measured exponent to be $\frac{1}{2}$. The measurements of Taylor *et al.*[13] are consistent with an exponent of $\frac{1}{3}$, although the data are not accurate enough to determine an accurate exponent.

The model predicts that the smectic *C* phase is biaxial with transverse anisotropy varying as $(T_c - T)$. The smectic *C* phase is biaxial; however, there have been no measurements of optical anisotropy versus temperature.

Durand[14] and co-workers have observed the thermally excited director fluctuations in the smectic *C* phase of di-(4-*n*-decyloxybenzal)-2-chloro-1-4-phenylene diamine. This material transforms from the nematic phase directly into the smectic *C* phase with a tilt angle of about 45°. The observed elastic constant ratio is about 2 to 1.

A twisted smectic *C* phase was suggested by Saupe[15] and observed by Helfrich and Oh.[16] With the present theory one would expect such a phase when there are asymmetric carbon atoms near the ends of both end chains and this is the case studied experimentally. Presumably one could produce a microscopic theory of the twisted smectic *C* phase similar to Goosens[17] theory of the cholesteric phase by incorporating into the present theory the van der Waals interactions of asymmetric carbon atoms on molecules in neighboring planes.

The available experimental evidence is qualitatively consistent with the physical properties of the ordered phase which was labeled smectic *C*. The theoretical model assumes that rotation of the molecule about its long axis freezes out in the smectic *C* phase and that the tilt angle passively follows the orientational order parameter. These experiments are also consistent with deGennes–Landau theory, which is based on the accepted picture of the smectic *C* phase as a tilted smectic *A* with no additional orientational order. In order to determine experimentally which physical picture is correct it is necessary to have experiments which probe the rotational motion of the molecules.

The calculation as presented is quasi-two-dimensional, with intraplanar interactions taken into account from the start and interplanar interactions grafted on at the end. This is a reasonable thing to do if the interplanar interactions are weak; if this is actually the case one would expect that the interplanar elastic constant C_{22} would be small and that critical exponents would be two-dimensional. The present experimental evidence, though weak, contradicts this. The observed critical exponent for the tilt angle is $\approx\frac{1}{3}$ (three-dimensional) rather than $\frac{1}{8}$ (two-dimensional), and the observed elastic constant anisotropy is 2. This does not invalidate the model but it is an indication that one needs to incorporate interplanar interactions into the model from the beginning.

VI. FACTORS AFFECTING THE STABILITY OF THE SMECTIC *C* PHASE

We would like to be able to use the theoretical model to discuss the relationship between molecular structure and the stability of the smectic *C* phase relative to the smectic *A* phase. The ultimate goal would be to calculate the transition temperature from the molecular structure. We will first attempt to calculate the transition temperature from the dipole-dipole interaction and then discuss the other factors which contribute to the smectic *C* stability.

In order to discuss intermolecular interactions one must first understand the molecular conformation in the liquid state. In the crystalline state the molecules are often in the all-trans configuration. (However, in para azoxyanisole[18] the ether oxygens are cis relative to the azoxy oxygen.) In Fig. 3, we show three molecules (in the all-trans configuration) which exhibit smectic *C* phases. The double bonds are drawn in to show that the central ring structures are conjugated and that the end chains are aliphatic. Pi bonding makes the central ring structures relatively rigid and the barriers to rotation about partial double bonds is relatively high. In the aliphatic end chains the rotational barriers are much lower and one has an appreciable occupation of gauche configurations, which makes the end chains flexible in the liquid. It is important to know the relative orientation of the dipole moments associated with

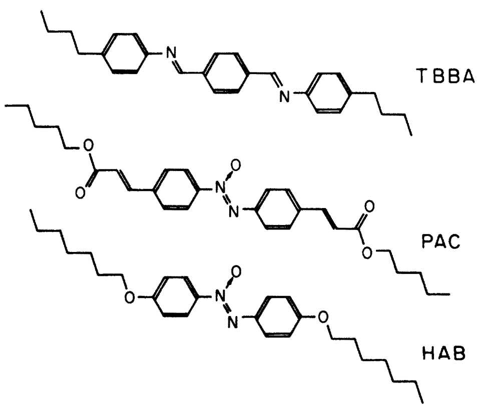

FIG. 3. All-trans structures of three liquid-crystal molecules exhibiting smectic *C* phases: terephthal-bis-butyl aniline (TBBA), *n*-pentyl-azoxy dicinnamate (PAC), and *n*-heptyloxy azoxy benzene (HAB). The actual conformations in the liquid-crystal phases are unknown.

the oxygen and nitrogen atoms in the molecule. In the all-trans configuration shown in Fig. 3 the outboard dipoles are approximately antiparallel and approximately perpendicular to the long axis. This is favorable for the smectic *C* phase. However, if the barriers to internal rotation for the bonds between the dipoles are not high enough, bond rotation can reverse one dipole in laboratory times (minutes or hours), and roughly half of one's molecules will have parallel outboard dipoles. This situation is less favorable for the smectic *C* phase. If the smectic *C* phase occurs anyway, the antiparallel dipole conformation will be preferred and the internal rotation will freeze out in the ordered phase. Whether or not internal rotation occurs must be decided in individual cases.

We will now ignore the conformational problem and calculate the transition temperature from the dipole-dipole interaction using the geometry of the all-trans configuration. We will first improve Eq. (60) somewhat by taking a more realistic intermolecular correlation function; we assume six nearest neighbors at a distance of $(2/\sqrt{3}n_2)^{1/2}$ and a uniform distribution for distances greater than $(7/\pi n_2)^{1/2}$. With this correlation function the transition temperature is reduced by 20% and we find

$$kT_c = 0.8\,\frac{\mu_2^2(\pi n_2)^{3/2}}{\epsilon_\infty}\,(1-Y^{-3})\,. \tag{72}$$

For TBBA (Fig. 3) there is a dipole moment[19] of 1.57×10^{-18} esu associated with the nitrogen in each Schiffs base linkage which is nearly perpendicular to the long axis with a dipolar separation of 7 Å. Taking $D\approx 5$ Å the $1-Y^{-3}$ term is 0.8; taking $n_2=4\times10^{14}$ cm^{-2} we find $kT_c=260$ °K compared with the experimental value of 445 °K. A similar calculation for PAC and HAB yields transition temperatures of 370 and 220 °K compared to experimental values of 411 and >360 °K. The dipole-dipole interaction evidently accounts for about half the interaction.

The molecular shape also contributes to the stability of the smectic *C* phase if the molecules are not cylindrical. In HAB (Fig. 3) the end chains are not collinear with the central body of the molecule, resulting in a zig-zag molecular shape. If the molecules rotate freely about the long axes, as in the smectic *A* phase, the end chains of neighboring molecules get crosswise and impair the translational motion of the molecules. In the ordered smectic *C* phase, however, the end chains are parallel and there is more freedom for translational motion. Thus the entropy of translational motion stabilizes the oriented phase in the smectic *C* case just as it does in the nematic case. This effect is obviously stronger for longer end chains, which explains the increased stability of the smectic *C* phase for higher members of an homologous series. In addition, the interaction of end chains of molecules in neighboring smectic planes is responsible for the interplanar interaction.

The model assumes that the smectic order is well established and neglects the thermal motion of the molecules normal to the planes (in the *z* direction). Thus if the dipole moments are symmetrically arranged about the molecular center the dipoles on neighboring molecules will be "in register" in the *z* direction and the interaction will be a maximum. The averaged dipole-dipole interaction will be reduced by thermal motion in the *z* direction and by having unsymmetrically placed dipoles. This thermal motion increases strongly near the smectic-nematic phase transition and it requires a strong interaction to maintain a material like HAB in the smectic *C* phase over the entire smectic range. The smectic order is stronger and thermal fluctuations weaker for higher homologs, which would explain part of the increased stability of the smectic *C* phase of higher homologs. The smectic *C* phase is apparently not observed in unsymmetrical compounds, but this effect has not been systematically explored.

The structural factors favoring the smectic *C* phase relative to the smectic *A* phase are then: (i) approximate center of symmetry; (ii) large outboard antiparallel dipole moments; (iii) zig-zag (trans) gross shape of molecule. It would be of great value at this point to have a thorough chemical study of the effects of various structural factors on the stability of the smectic *C* phase.

VII. CONCLUSIONS

We have introduced a molecular model with dipole-dipole interactions and have shown that it leads to three orientationally ordered phases, one of which has the physical properties of the smectic *C* phase. In this model the molecular tilt follows the orientational order parameter. This physical picture of the smectic *C* phase is distinct from the accepted view of a smectic *C* as a tilted smectic *A*. If one measures properties associated with the tilt angle both pictures lead to the same experimental results. To my knowledge there is no experimental evidence that the rotationally ordered picture is correct. The microscopic theory is based on well-known interactions and is certainly plausible; it is also the only microscopic theory we have. Nonetheless it is obviously highly desirable to have measurements of properties associated with molecular rotation to confirm the basic physical picture.

One would like, in fact, to have a variety of experiments on a material which exhibits a smectic-*A*–smectic-*C* phase transition. TBBA is an unfortunate choice of material because it deteriorates at the high temperature of this transition. One would like to see thermal and optical measurements, and light scattering experiments. Of particular interest would be NMR measurements with a probe which couples to the orientational order parameter β, and dielectric loss measurements to observe the rotational relaxation of a molecule with a net dipole moment.

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