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# Molecular theory of the smectic $E$, $H$, and VI phases*

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The molecular theory of the smectic $B$ and $H$ phases is extended to the smectic $E$ and VI phases by including the phenyl-phenyl interaction in addition to the dipole-dipole potential used previously. This phenyl-phenyl interaction contains quadrupole-quradrupole, dispersive, and exchange terms. The possibility of both dipolar and "herringbone" order is considered in the self-consistent–field approximation. Four phases are found, all with a two-dimensional hexagonal lattice assumed: (1) a disordered phase (smectic $B$); (2) an oriented phase in which dipoles align (smectic $H$); (3) a herringbone phase with phenyl groups ordered (smectic $E$); (4) and a herringbone phase with both phenyl groups and dipoles ordered (smectic VI). In the phases with dipolar order the director is tilted with respect to the normal to the plane. The transitions vary in order. The temperature dependence of the order parameters, entropy, and specific heat are computed.

## I. INTRODUCTION

It has been known for almost a century that certain organic molecules have additional phases between the usual isotropic-liquid phase and the crystalline phase. The phases are usually called the liquid-crystal phases.

The least ordered of the liquid-crystal phases is the nematic, in which the long axes line up parallel to a preferred axis in space, the director. Maier and Saupe[1] introduced a molecular model for the interactions between anisotropic molecules, and solved this model in the mean- or self-consistent-field approximation.

In the smectic $A$ phase, the long molecular axes lies parallel to an axis in space and the molecular centers lie on equidistant planes perpendicular to this axis (Fig. 1). Given the nature of this order, Kobayashi[2] and McMillan[3] have been able to formulate microscopic theories in terms of intermolecular potentials. In addition, there are also Landau theories of the smectic $A$ phase.[4,5]

In the smectic $C$ phase, the director is tilted with respect to the smectic plane normal. DeGennes[6] has proposed a Landau theory using the tilt angle as the order parameter. McMillan[7] has formulated a microscopic theory using the molecular dipole-dipole interaction and permitting orientational order of the dipoles. The oriented phase is tilted and has the physical properties of the smectic $C$ phase. The parameters of the model can be approximately related to those of the molecular structure. This orientational order has been confirmed experimentally by recent NMR measurements.[8]

The smectic $B$ and $H$ phases are characterized by a two-dimensional hexagonal lattice within each smectic plane. In the $H$ phase the director is tilted, while in the $B$ phase it isn't.[9] In a recent paper McMillan and the author[10] proposed a model of the $B$ and $H$ phases based on a soft-core repulsive potential and a dipole-dipole intermolecular potential, allowing both translational or orientational order. As in the theory of the $C$ phase, the dipole term can be related to molecular structure.

Recent x-ray studies[11] have shown that a phase, the smectic VI phase, is characterized by a two-dimensional hexagonal lattice and tilting of the long molecular axis with respect to the plane normal. Unlike the $H$ phase, however, this substance exhibits herringbone symmetry (see Fig. 2). This herringbone pattern was previously proposed for the $B$ phase.[12] There is also evidence,[13] that the smectic $E$ phase has a two-dimensional hexagonal lattice and herringbone pattern, but untilted director.

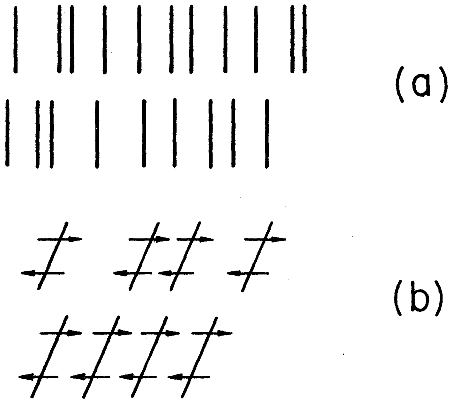

FIG. 1. (a) Molecular order in the smectic $A$ phase. Molecules are free to rotate around the long axis. (b) Molecular order in the smectic $C$ phase with dipoles aligned.

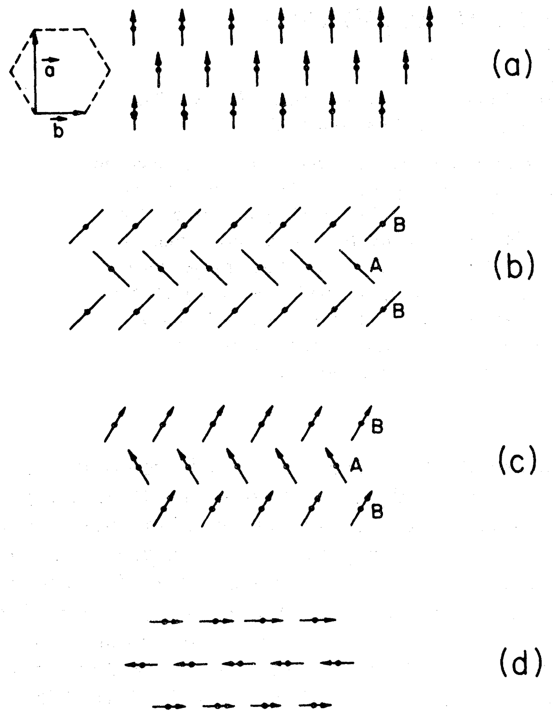

FIG. 2. (a) Hexagonal aligned structure of the smectic *H* phase. In the smectic *B* phase the dipoles are unaligned. (b) Ordered structure of the smectic *E* phase. The line represents the "axis of symmetry" perpendicular to the plane of the molecular phenyl rings. The dipoles are randomly oriented. The two types of sites are labeled. (c) Molecular order in the smectic VI phase. Both dipoles and phenyl groups are ordered. (d) "Antiferroelectric" phase which may result when dipoles are separated by less than a critical distance.

In this paper a microscopic theory is presented which includes the smectic *E* and VI phases, in addition to the *B* and *H* phases. The smectic *B* order is assumed well established; i.e., the hexagonal lattice is well defined, the director is normal to the plane, and the molecular centers sit on the plane. We assume an intermolecular potential due to a dipole-dipole interaction, and a phenyl-phenyl interaction. Interplanar interactions are ignored. These have been considered by other investigators.[14-16]

The model predicts three ordered phases in addition to one disordered phase. The transitions vary in order. Many of the physical and optical characteristics agree with experiment.[17,18]

The plan of this paper is as follows. In Sec. II we discuss the relevant intermolecular forces, i.e., the multipole-multipole, Van der Waals, and exchange interaction. The relation to molecular structure is discussed, and an order-of-magnitude estimate for the coupling constants is given. In Sec. III the theoretical model is presented and solved within the mean- or self-consistent-field approximation. The self-consistency equations for the order parameters are derived and the energy, entropy, and free energy found in terms of the order parameters. Section IV presents the method of numerical solution for the order parameters and the results of this calculation. In Sec. V we discuss the shortcomings of the model.

## II. INTERMOLECULAR FORCES

A typical liquid crystal molecule, TBBA, is shown in Fig. 3(a). This material has smectic *A*, *C*, *H*, and VI phases. In this paper we will use the TBBA molecule as a basis for the discussion of intermolecular forces in organic crystals. Throughout this section terms independent of angle of rotation in a smectic plane will be dropped. Phenyl-phenyl interactions between a molecule and its six equidistant nearest neighbors in a layer will be considered. Dipole-dipole interactions will be kept to third-nearest neighbors. Interplanar interactions are ignored throughout this paper. The validity of this is discussed by deGennes and Sarma.[14,15]

### A. Multipole-multipole interactions

McMillan[7] has discussed the permanent dipole moments $\mu$ associated with the nitrogen in each

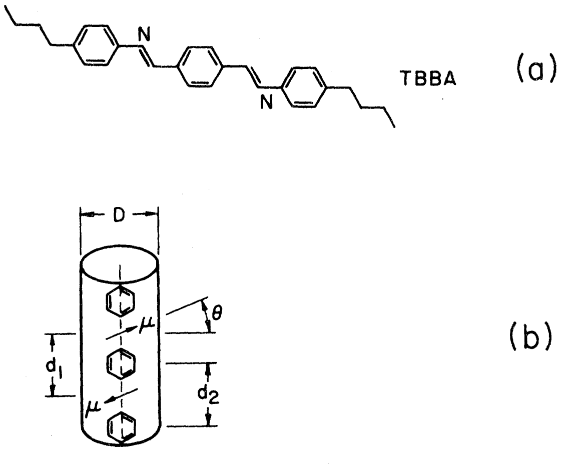

FIG. 3. (a) The compound terephthal-bisbutyl aniline (TBBA) exhibits smectic *A*, *C*, *H*, and VI phases. The all-*trans* structure is shown. The actual configuration is not known. (b) Molecular model: a cylindrical shape of length *L* and diameter *D*, the two dipoles $\mu$ are a distance $d_1$ apart, and the phenyl groups are separated by a distance $d_2$.

Schiff's-base linkage in TBBA. There are also other strong multipoles in the molecule. Each phenyl group contributes a large quadrupole moment $\Theta$. The magnitude of this quadrupole is not known. It could be estimated by the value of the benzene quadrupole. Unfortunately, the value of the benzene quadrupole is subject to controversy. Probably the best value is that of Rae and Mason,[19] $\Theta = -8.8\times10^{-26}$ esu.

If the aliphatic chains at each end of the molecule were ordered, these would also contribute a permanent quadrupole moment. There is evidence,[16] though, that these chains rotate around the single bonds, and so make no contribution.

The multipole-multipole interaction as usually shown in the literature[20,21] is given by

$$U_{1,2}^{\text{multipole}} = U_{1,2}^{\text{D-D}} + U_{1,2}^{\text{D-Q}} + U_{2,1}^{\text{D-Q}} + U_{1,2}^{\text{Q-Q}} , \qquad (1)$$

where

$$U_{1,2}^{\text{D-D}} = \mu_1\mu_2 R^{-3}[2\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2] ,$$

$$U_{1,2}^{\text{D-Q}} = \tfrac{3}{2}\mu_1\Theta_2 R^{-4}[\cos\theta_1(3\cos^2\theta_2 - 1) + \sin\theta_1(2\cos\theta_2\sin\theta_2)] ,$$

$$U_{1,2}^{\text{Q-Q}} = \tfrac{3}{4}\Theta_1\Theta_2 R^{-5}[1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 + 17\cos^2\theta_1\cos^2\theta_2 + 2\sin^2\theta_1\sin^2\theta_2 + 16\sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2] .$$

The angles $\theta_1$ and $\theta_2$ are defined in Fig. 4(a). For computation it is more convenient to define all angles from a fixed direction in the plane, as shown in Fig. 4(b). The benzene-ring angles give the position of the axis of the ring, as is usual in the literature cited.

The distance between neighbors $D$ is less than the distance between dipoles on the same molecule $d_1$ and between quadrupoles $d_2$, so that interactions between multipoles of the same order on different levels may be neglected. The dipole-quadrupole interaction can be shown to vanish when the sum over neighbors is done.

### B. Van der Waals interactions

The Van der Waals or dispersive interaction has already been used by Maier and Saupe[1] to explain the alignment of the long axes of organic molecules in the nematic phase. The dispersive force will also contribute to rotational alignment of molecules within a smectic plane.

Again, the aliphatic tails probably make little or no contribution to the interaction because of their random rotational motion. The phenyl or benzene groups make the major contribution to angular order in a smectic plane.

The dispersive interaction between two cylindrically symmetric benzene rings has been discussed by Banerjee and Salem.[22] The interaction can be written as

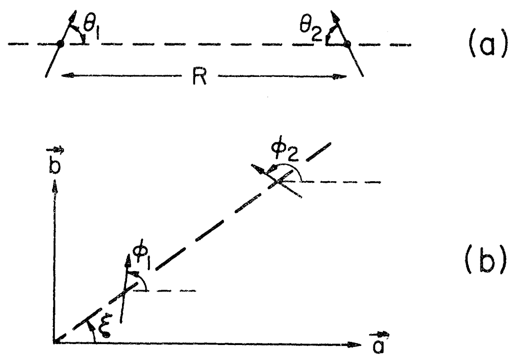

FIG. 4. (a) Coordinate system usually used in literature. For phenyl interactions the arrow lies along the axis of "cylindrical" symmetry of the ring. (b) More convenient coordinate system fixed to hexagonal lattice vectors $\vec{a}$ and $\vec{b}$.

$$U_{1,2}^{\text{disp}} = -R^{-6}C(\theta_1, \theta_2) , \qquad (2)$$

where

$$C(\theta_1, \theta_2) = (A - 2B + C)[4\cos^2\theta_1\cos^2\theta_2 + \sin^2\theta_1\sin^2\theta_2 - 4\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2] + 3(B - C)(\cos^2\theta_1 + \cos^2\theta_2) + (2B + 4C) . \qquad (3)$$

The angles in the smectic plane $\theta_1$ and $\theta_2$ are defined in Fig. 4(a). From Banerjee and Salem we calculate $A = 2.67\times10^2$, $B = 4.36\times10^2$, and $C = 7.33\times10^2$ a.u.

### C. Exchange interaction

The interaction between two molecules due to exchange of electrons from one molecule to another is both the strongest, and the most difficult to handle, of all the interactions discussed. An exact treatment is extremely difficult even for simple molecules.

A phenomenological potential of the form $U_{ij} = A_{ij}\exp(-r_{ij}/\rho_{ij})$ has been proposed for the exchange interaction by Williams[23,24] and Kitajgorodsky.[25,26] In this potential the atom $i$ belongs to molecule 1 and atom $j$ to molecule 2, $r_{ij}$ being approximately the interatomic distance. The total intermolecular potential is due to the sum over all atoms in each molecule. The constants $A_{ij}$ and $\rho_{ij}$ depend only on the nature of the two atoms. For example, we have $A_{\text{CC}}, A_{\text{CH}}, A_{\text{HH}}$. Williams[23] has found values of the $A$'s and $\rho$'s by a statistical fit of 77 equations for 9 aromatic hydrocarbons. Unfortunately, quadrupole and other multipole terms are combined with the exchange term; this makes this treatment questionable.

For TBBA we should get sizable contributions to exchange interaction energy, at fixed distance between the two molecules, from the three benzene groups, and from the two Schiff's-base linkages. The three benzenes have a total of 12 interacting hydrogens and 12 interacting carbons from each TBBA molecule, while we only get two hydrogens and two nitrogens contributing from the Schiff's-base linkages. All interactions being equal, the Schiff's-base linkages would only contribute $\frac{1}{24}$ as much to the interaction energy as the rings. Actually the contribution may be less. The Schiff's-base contribution will be ignored.

It is easy to approximate the actual interaction by dropping all C-H terms. In general, this isn't valid, but Williams has shown that the energy of rotation around a para-axis across the benzene ring is mainly determined by the H-H terms, only 20% of the energy coming from C-H terms. After dropping C-H terms and doing the sums of all C-C and H-H over two benzene rings constrained to rotate in a plane, with axis of rotation for each ring through opposite carbon atoms, the potential can be approximated by

$$U^{\mathrm{exc}}_{1,2} = C_1 \cos^2\theta_1 \cos^2\theta_2 + C_2(\cos^2\theta_1 + \cos^2\theta_2) + C_3 \sin^{2N}\theta_1 \sin^{2N}\theta_2 \ . \qquad (4)$$

The numbers $C_1$, $C_2$, and $C_3$ can be found by fitting the numerical data. The term $C_3 \sin^{2N}\theta_1 \sin^{2N}\theta_2$, with $N \approx 13$, is a hard-core repulsive term, $C_3$ being $\sim 10^2$ times as large as the other coefficients. This hard-disk term is only important when the two benzene rings are approximately coplanar. At other angles, $C_1$ and $C_2$ determine the energy. Numerically, $C_1 \sim 1\times10^{-13}$, $C_2 \sim -1\times10^{-13}$, and $C_3 \sim 2\times10^{-11}$ erg at an intermolecular distance of 5.2 Å. The fit can probably be improved by adding other terms to the potential.

In this section the various contributions to the intermolecular potential in organic hydrocarbons have been briefly discussed. The importance, and even the form of each of the three contributions, is still a matter of controversy and research. They have been mentioned here for two reasons: (i) the coupling constants of each of these terms in determining the angular orientation of liquid-crystal molecules within a smectic plane are approximately equal. Estimates of the important coupling constants are all on the order of $10^{-13}$ erg; (ii) to motivate the form for our average or mean field operating on each molecule. These reasons will become clearer in the next section.

## III. THEORETICAL MODEL

We consider one plane of a perfectly ordered smectic $B$ liquid crystal, call it the $xy$ plane. In this plane the rodlike molecules have their long axes aligned, and the molecular centers are arranged in a two-dimensional hexagonal lattice in the $xy$ plane. The rotational phase transitions of the two-dimensional hexagonal smectic phases will be explored.

Consider the following model of a liquid-crystal-forming molecule, which is a modification of the model proposed by McMillan[7] in his theory of the smectic $C$ phase, and used by Meyer and McMillan[10] in a theory of the smectic $B$ and $H$ phases [see Fig. 3(b)]. The molecule is assumed to be a long rod with oppositely oriented dipoles tilted at an angle on opposite sides of the molecular center. Along the axis are a number of phenyl or benzene groups, which are assumed to be all coplanar. The relative positions of these elements are fixed; i.e., all internal rotations are frozen out. The validity of these assumptions will be discussed in Sec. V.

The intermolecular potential is taken to be

$$U_{12} = U_{12}^{\text{multipole-multipole}} + U_{12}^{\text{disp}} + U_{12}^{\text{exc}}, \qquad (5)$$

where the contributions of (5) are given by Eqs. (1), (2), and (4), respectively. Only nearest-neighbor interactions are treated in the phenyl-phenyl term. The hard-disk term in Eq. (4) will be ignored. This term is discussed in Sec. V.

We now wish to solve the model within the self-consistent-field approximation. To do this we first assume that each molecule moves in an average potential $V$ at its site. This is complicated in this case by the fact that, although all sites are equivalent in the smectic $B$ and $H$ phases (see Fig. 2), there are two different kinds of sites in the smectic $E$ and VI phases (see Fig. 2). Label these sites type $A$ and $B$ as shown in the figure.

On all $A$ sites, assume the molecule feels the average potential

$$V_A(\phi_1) = +V_0\gamma(\cos^2\phi_1 - \tfrac{1}{2}) + V_1\alpha\cos\phi_1\sin\phi_1 - V_2\beta\cos\phi_1 - V_3\delta\sin\phi_1 \ . \qquad (6)$$

Make the further assumption that $V_A$ and $V_B$ are related by

$$V_A(\phi) = V_B(-\phi) \ . \qquad (7)$$

The order parameters $\alpha$ and $\gamma$ show the degree of "herringbone" order, and are nonzero in the smectic $E$ and VI phases [see Figs. 2(b) and 2(c), respectively]. If we just consider the upper dipoles on a smectic layer, the order parameter $\beta$ gives the degree of "ferroelectric" order in the $\vec{a}$ direction [see Fig. 2(a)]. Because of the lower dipoles, there is no net moment. The order parameter $\delta$ reflects the degree of "antiferroelectric" order in the $\vec{b}$ direction [see Figs. 2(c) and 2(d)]. The order parameter $\beta$ is nonzero in the smectic

$H$ and VI phases, and $\delta$ is nonzero in the smectic VI phase only.

With the one-particle potentials given by Eqs. (6) and (7), the (unnormalized) one-particle distribution functions of the two types of sites are

$$f_A(\phi_1) = \exp[-V_A(\phi_1)/kT] \tag{8a}$$

and

$$f_B(\phi_1) = \exp[-V_B(\phi_1)/kT] \ . \tag{8b}$$

The average value of a function $G(\phi_1, \phi_2, \phi)$ at a site of type $I$ can be defined by

$$\overline{G}_I(\phi_1) = Z^{-1}\sum_n \int_{-\pi}^{\pi} d\phi_n \, G(\phi_1, \phi_n, \xi_n) f_n(\phi_n) \, , \tag{9}$$

where the sum is over neighbors of type $n$ around $I$, and where

$$Z = \int_{-\pi}^{\pi} d\phi_2 f_A(\phi_2) = \int_{-\pi}^{\pi} d\phi_2 f_B(\phi_2) \ ,$$

and the angles $\phi_1$, $\phi_2$, and $\xi$ are defined in Fig. 4(b). Also define

$$\langle G(\phi_2)\rangle = Z^{-1}\int_{-\pi}^{\pi} \exp[-V_A(\phi_2)/kT] \, G(\phi_2) \, d\phi_2 \ .$$

Using the two-body potentials (1), (2), and (4), expressed in terms of $\phi_1$, $\phi_2$, and $\xi$, the average potential which one molecule feels is calculated from the two-body potential by averaging over all the neighbors:

$$\overline{V}_A(\phi_1) = Z^{-1}\sum_n \int_{-\pi}^{\pi} d\phi_n \, U_{1,n}(\phi_1, \phi_n, \xi_n) f_n(\phi_n) \ . \tag{10}$$

The generalization of $\overline{V}_B(\phi_1)$ is obvious. If we calculate the nearest-neighbor dipole-dipole contribution to $\overline{V}_A(\phi_1)$ from Eq. (10), we find

$$\overline{V}_A^{\text{D-D}}(\phi_1) = -6\mu^2 D^{-3}\cos\phi_1\langle\cos\phi_2\rangle - 10\mu^2 D^{-3}\sin\phi_1\langle\sin\phi_2\rangle \ . \tag{11}$$

In this equation there is a factor of 2 due to two dipoles per molecule.

The dipole-quadrupole term in Eq. (1) vanishes when we do the sum over neighbors.

For self-consistency of Eqs. (11) and (6), we must set

$$V_2 = 6\mu^2 D^{-3} \ , \tag{12a}$$

$$V_3 = -10\mu^2 D^{-3} \ , \tag{12b}$$

$$\beta = \langle\cos\phi_2\rangle \ , \tag{12c}$$

$$\delta = -\langle\sin\phi_2\rangle \ . \tag{12d}$$

If we now include the contribution of the second- and third-nearest neighbors to $V_2$ and $V_3$, we find that Eqs. (12a) and (12b) are modified slightly to give

$$V_2 = 7.9\,\mu^2 D^{-3} \tag{12a$'$}$$

and

$$V_3 = -7.05\,\mu^2 D^{-3} \tag{12b$'$}$$

The formulas for the order parameters are unchanged.

The relatively long range of the dipole-dipole interaction makes it necessary to include these second- and third-nearest-neighbor terms to get a reasonable phase diagram. In fact, if $V_3 < -V_2$, as predicted by Eqs. (12a) and (12b), the $H$ phase will be unstable and the stable phase will be an "antiferroelectric" phase, as shown in Fig. 2(d). This should happen when $d/D$ is smaller than a critical value $(d/D)_{\text{cr}}$, but for a complete discussion of this, the entire two-dimensional lattice sum must be performed. This "antiferroelectric" phase is untilted and biaxial. The necessary lattice sums are not performed here.

The dispersive, quadrupole-quadrupole, and exchange interactions contribute terms of the form $(\cos^2\theta_1 + \cos^2\theta_2)$, $\cos^2\theta_1\cos^2\theta_2$, and $\cos\theta_1\cos\theta_2\sin\theta_1\sin\theta_2$. The dipole-quadrupole term vanishes completely when the sum in Eq. (9) is performed. The other terms contribute two terms which are nonvanishing. When expressed in $\phi_1$, $\phi_2$, and $\xi$, these are of the form

$$U_{1,2}^{\text{phenyl-phenyl}} = A_1\cos^2(\phi_1 - \phi_2) + A_2\cos(4\xi)\cos(2\phi_1 + 2\phi_2) \ . \tag{5a}$$

This could be viewed as a phenomenological phenyl-phenyl interaction. When the lattice is not truly a two-dimensional hexagonal array, an additional term

$$U_{1,2}^{\text{distortion}} = A_3\cos(2\xi)(\cos 2\phi_1 + \cos 2\phi_2) \tag{5b}$$

is nonvanishing due to lack of symmetry, and must be added to the phenyl-phenyl potential. This resembles an "external field" fixed to the lattice. The self-consistent treatment of such an external field is given by McMillan[4] and will not be discussed here.

We will evaluate the contribution to $\overline{V}_A$ due to $U^{\text{phenyl-phenyl}}$ for nearest neighbors only, due to the short range of the interaction involved:

$$\overline{V}_A(\phi_1) = 6A_1(\cos^2\phi_1 - \tfrac{1}{2})\langle\cos 2\phi_2\rangle - (2A_1 + 8A_2)(\cos\phi_1\sin\phi_1)\langle\sin 2\phi_2\rangle \ .$$

For self-consistency of the equations above Eq. (6), it is necessary to set

$$\alpha = -\langle\sin 2\phi_2\rangle \tag{13a}$$

and

$$\gamma = \langle\cos 2\phi_2\rangle \ . \tag{13b}$$

The coupling constants are given by $V_0 = 6A_1$ and $V_1 = 2A_1 + 8A_2$. Specifically, for the quadrupole-quadrupole term

$$V_0^{\text{Q-Q}} = \tfrac{27}{8} n\Theta^2 R^{-5}, \tag{14a}$$

$$V_1^{\text{Q-Q}} = \tfrac{219}{8} n\Theta^2 R^{-5}, \tag{14b}$$

where $\Theta$ is the mean quadrupole moment of the phenyl group, treated as if the ring were cylindrically symmetric, and $n$ is the number of ordered phenyl groups per molecule. If a phenyl group is free to rotate within the molecule, it doesn't contribute to $n$.

If the approximation of cylindrical symmetry isn't valid, $\Theta$ may be replaced by $(\Theta_{xx} - \Theta_{yy})$. This also extends the validity to cases where more complex ring structures occur in the molecule. For $\Theta = 9 \times 10^{-26}$ esu, the value of $\Theta_{\text{benzene}}$ calculated by Rae and Mason, we find $V_0^{\text{Q-Q}} = 8.4 \times 10^{-14}$ erg and $V_1^{\text{Q-Q}} = 6.8 \times 10^{-13}$ erg for TBBA.

The Van der Waals contributions are

$$V_0^{\text{disp}} = -\tfrac{27}{2} nR^{-6}\{A - 2B + C\}, \tag{15a}$$

$$V_1^{\text{disp}} = -\tfrac{11}{2} nR^{-6}\{A - 2B + C\}, \tag{15b}$$

where $A$, $B$, and $C$ are defined in Eq. (3). Estimates of $A$, $B$, and $C$ based on the work of Banerjee and Salem[22] for benzene give $V_0^{\text{disp}} = -8.4 \times 10^{-14}$ erg and $V_1^{\text{disp}} = -3.4 \times 10^{-14}$ erg. Note that these coupling constants are both negative.

Finally, the exchange interaction in the form of Eq. (4) gives

$$V_0^{\text{exc}} = V_1^{\text{exc}} = \tfrac{3}{2} nA, \tag{16}$$

where $A$ is determined by fitting Eq. (4) to the results of a sum of interatomic potentials. An estimate gives $V_0^{\text{exc}} = V_1^{\text{exc}} = 4 \times 10^{-13}$ erg.

The smectic $B$-$E$ and smectic $B$-$H$ transitions are both second order, and the transition temperatures may be easily calculated on the basis of the self-consistency equations (12c), (12d), and (13).

The smectic $B$-$E$ transition is easiest to calculate because there is only one nonzero order parameter $\alpha$ in the smectic $E$ phase. If we compute $\langle 2\cos\phi \sin\phi\rangle$ we find, keeping only terms of second order in both numerator and denominator,

$$\alpha = [\tfrac{1}{4}(V_1/kT) - 1]^{1/2}(4kT/V_1), \tag{17}$$

so that

$$kT_c^{B-E} = \tfrac{1}{4} V_1 . \tag{18}$$

Note that no $B$-$E$ transition can take place for a purely dispersive interaction.

The smectic $B$-$H$ transition can be calculated in the same way, except that in the smectic $H$ phase the parameters $\beta$ and $\gamma$ are both nonzero, while $\alpha = \delta = 0$. We can simplify the calculations if we use $\gamma \ll \beta$. Ignoring all $\gamma$ terms in the $\beta$ [Eq. (12c)], we find

$$\beta = (2kT/V_2)[\tfrac{1}{2}(V_2/kT) - 1]^{1/2} \tag{19}$$

and

$$kT_c^{B-H} = \tfrac{1}{2} V_2 . \tag{20}$$

Similarly, the $\gamma$ equation gives, to the lowest orders in both $\beta$ and $\gamma$,

$$\gamma = -\tfrac{1}{4}\gamma(V_0/kT) + \tfrac{1}{8}\beta^2(V_2/kT)^2 . \tag{21}$$

Clearly, $\gamma \sim \beta^2 \sim (T_c^{B-H} - T)^1$.

In order to determine which phase is stable at a given temperature, we must calculate the free energy of the system. The entropy per molecule of a type $A$ site is given by

$$\begin{aligned} -TS_A &= kT\langle \ln e^{-V_A/kT}\rangle - kT \ln Z \\ &= -2N^{-1}\langle V_A(\phi)\rangle - kT \ln Z . \end{aligned} \tag{22}$$

The internal energy is just the thermodynamic average of the two-particle interaction

$$U_A = \tfrac{1}{2}N \sum_n \langle\langle U_{A,n}^{12}\rangle_A\rangle_n = \tfrac{1}{2}N\langle V_A(\phi)\rangle .$$

This gives the internal energy per molecule

$$N^{-1}U_A = \tfrac{1}{4}\gamma^2 V_0 - \tfrac{1}{4}\alpha^2 V_1 - \tfrac{1}{2}\beta^2 V_2 + \tfrac{1}{2}\delta^2 V_3 . \tag{23}$$

The free energy is given by $F_A = U_A - TS_A$. The self-consistency equations (12c), (12d), and (13) can also be found by minimizing the free energy with respect to the order parameter.

Finally, the specific heat at constant volume is given by

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V . \tag{24}$$

Now we have everything we need to calculate the thermodynamic behavior of the model.

McMillan[7] has derived an expression for the tilt angle as a function of temperature for the smectic $C$ phase. A similar expression can be derived for the smectic $H$ and VI phases. If third-nearest-neighbor terms are kept, from Eq. (9) we can evaluate the average $x$ component of the electric field on an $A$ site and find $\overline{E}_x \cong 3.96\mu\beta D^{-3}$. Then the torque to tilt the molecule in the $x$ direction is $2.64\beta\theta kT_c^{B-H}$. There will be a restoring torque proportional to the tilt angle. Equating torques, we find the tilt angle to be $2.64\beta\theta kT_c^{B-H}K^{-1}$, where $\theta$ is the deviation of the dipole moment from perpendicular to the molecular axis, and $K$ is an elastic constant characteristic of the material.

The coupling to dipoles on different levels has been ignored throughout this section. McMillan[7] has shown how the effects of dipoles on other levels can be included.

By considering the angle of rotation of the molecules in a smectic plane, it can be shown that the smectic VI phase of the model is optically biaxial, while the *E* phase is optically uniaxial. However, distortions of the two-dimensional hexagonal lattice can make the *E* phase of the model weakly biaxial.

In summary, in this section we have treated the intermolecular interaction $U_{12}$ in the mean-field approximation, and have found the four order parameters of the model. It has been shown that the transition temperatures of the *B*-*E* and *B*-*H* transitions are easily given in terms of the coupling constants of the effective one-body potentials. The energy, free energy, entropy, and specific heat have been found in terms of the order parameters.

## IV. NUMERICAL RESULTS

In this section we will solve the self-consistent equations [(12c), (12d), and (13)] for the order parameters. As we saw in Sec. III, it is an easy step from there to find the entropy, free energy, energy, and specific heat.

In order to solve the four coupled self-consistent equations, we only need to be able to perform the integrations over $\phi$. These were done numerically using Simpson's rule and keeping 100 points in the interval from $-\pi$ to $\pi$.

Since the smectic VI phase has four order parameters, this is the most difficult to solve, and will be described here. All other phases can be solved by simplifications of this process. The procedure is essentially the Newton method in four dimensions. First, choose values of all the coupling constants and a fixed value of the reduced temperature $t = T/T_c^{B-H}$ (in this section we will always use the reduced temperature). Then choose trial values of $\alpha^T/t$, $\beta^T/t$, $\gamma^T/t$, and $\delta^T/t$. The self-consistency equation can now be cast in the form

$$f_1\left(\frac{\alpha}{t},\frac{\beta}{t},\frac{\gamma}{t},\frac{\delta}{t},t\right)=g_1\left(\frac{\alpha}{t},\frac{\beta}{t},\frac{\gamma}{t},\frac{\delta}{t}\right)-\left(\frac{\alpha}{t}\right)t=0\,, \tag{25a}$$

$$f_2\left(\frac{\alpha}{t},\frac{\beta}{t},\frac{\gamma}{t},\frac{\delta}{t},t\right)=g_2\left(\frac{\alpha}{t},\frac{\beta}{t},\frac{\gamma}{t},\frac{\delta}{t}\right)-\left(\frac{\beta}{t}\right)t=0\,, \tag{25b}$$

and similarly for $\gamma$ and $\delta$.

For the trial values of the arguments, Eq. (25) will not be satisfied. Each trial value will be related to the true root of the equations by

$$(\alpha/t)^T=\alpha/t-\epsilon_1\,, \tag{26a}$$

$$(\beta/t)^T=\beta/t-\epsilon_2\,, \tag{26b}$$

and so on. We have four linear equations in four unknowns

$$\epsilon_1\frac{\partial f_i}{\partial(\alpha/t)}\left(\frac{\alpha^T}{t},\frac{\beta^T}{t},\frac{\gamma^T}{t},\frac{\delta^T}{t},t\right)+\cdots\epsilon_4\frac{\partial f_i}{\partial(\delta/t)} =-f_i\left(\frac{\alpha^T}{t},\frac{\beta^T}{t},\frac{\gamma^T}{t},\frac{\delta^T}{t},t\right), \tag{27}$$

where $i=1,\ldots,4$.

This gives us a set of four equations in $\epsilon_1$, $\epsilon_2$, $\epsilon_3$, and $\epsilon_4$.[27] These can be solved, and a new set of trial solutions found from Eqs. (26). This process can be iterated until the desired self-consistency is achieved. Commonly, only three iterations are necessary to get order parameters good to seven to ten decimal places. The derivatives in Eq. (27) are easily evaluated numerically.

Given the order parameters, the energy, entropy, and free energy are easily evaluated using the results of the previous section.

The process can be repeated at a different temperature and the specific heat evaluated by Eq. (24). Near the transition temperature we must compare the free energy to establish which phase is stable.

Define the parameter $R=V_0/V_1$. Since our intermolecular potential is a mixture of multipole-multipole, Van der Waals, and exchange terms, we don't know the value of $R$. In this section we choose $R=0.12$, the value for a pure quadrupole-quadrupole interaction, for convenience. The results are not significantly changed for other values of $R$. The values of $V_2$ and $V_3$ are those found by including out to third-nearest-neighbor terms in the dipole-dipole interaction.

The transition temperatures as a function of $V_1/kT^{B-H}$ are shown in the phase diagram in Fig. 5. The smectic *B*-*H* and *B*-*E* transitions are always second order, while the *B*-VI and *E*-VI transitions are always of first order. The smectic-*H*–smectic-VI transition may be of either order, and the theory predicts a tricritical point. To illustrate these behaviors, we plot in Figs. 6–9 the order parameters, entropy, and specific heat vs $t$ for $R=0.12$. In each case, the values of $V_1/kT^{B-H}$ are chosen to represent typical phase transitions corresponding to different orientational order of the two-dimensional hexagonal lattice. In Table I the order parameters of the phases are summarized.

In Sec. V we will give a discussion of the properties of the model and discuss the approximations and problems inherent in the model.

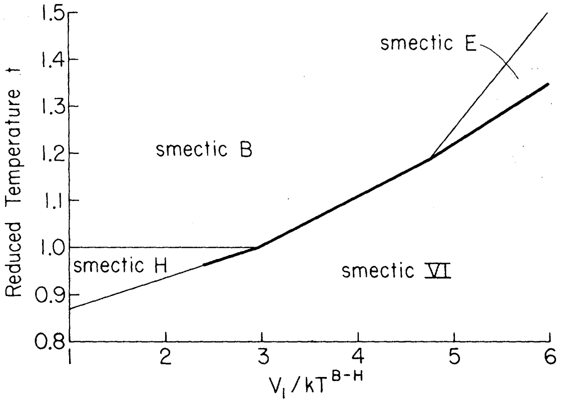

FIG. 5. Phase diagram of the theoretical model showing transition temperature in reduced units $(T/T_{BH})$ vs $(V_1/kT_{BH})$ for $V_0/V_1=0.12$. The heavy line represents a first-order phase transition, the lighter line a second-order transition.

## V. DISCUSSION

The connection between herringbone order and the interaction of phenyl groups has been noted independently by deVries.[28] In view of the analysis of Sec. III, though, his stress on the Van der Waals interaction, as opposed to the multipole and exchange terms, is probably incorrect.

The importance of the phenyl groups in the herringbone phases is supported by the precise x-ray analysis of Cox *et. al.*[29] on the crystalline structure of benzene. This is made especially clear by Fig. 1 of Cox (1932), which shows the herringbone structure of benzene crystals.

Comparison with experiment is difficult at this stage because of the lack of data on the *E* and VI phases. However, from Fig. 7 we expect $\Delta S^{H\text{-VI}} \sim 0.22R_0$. The entropy of the *H*-VI transition of TBBA has been determined to be $\Delta S_{\text{expt}}^{H\text{-VI}}=0.34R_0$.[30] This should be taken only as an order-of-magnitude comparison, since $V_1$ and $V_0$ for TBBA are both unknown.

It is worthwhile to list some of the assumptions and approximations which we have made. (i) We have worked within the mean-field approximation,

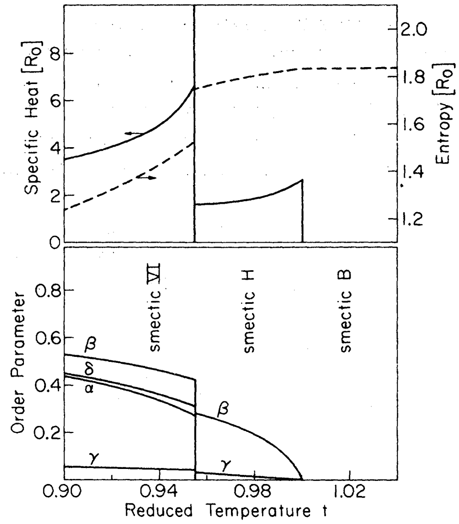

FIG. 7. Order parameters, entropy, and specific heat vs reduced temperature, showing the second-order smectic *B*-*H* and a first-order *H*-VI transitions, for $V_1/kT_c^{BH}=2.5$.

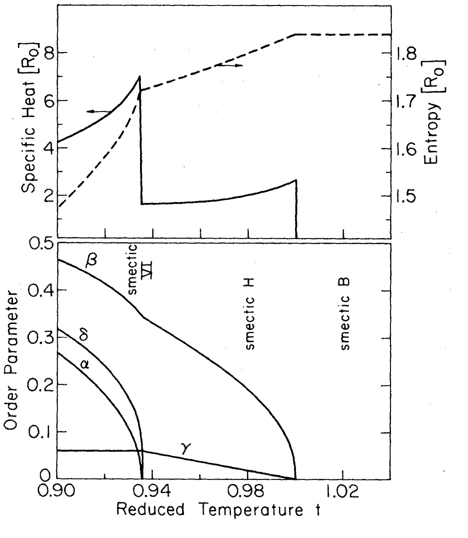

FIG. 6. Order parameters $\alpha$, $\beta$, $\gamma$, $\delta$, entropy $S$, and specific heat $C_v$ vs reduced temperature, showing the second-order smectic *B*-*H* and *H*-VI transitions, for $V_1/kT_c^{BH}=2.0$.

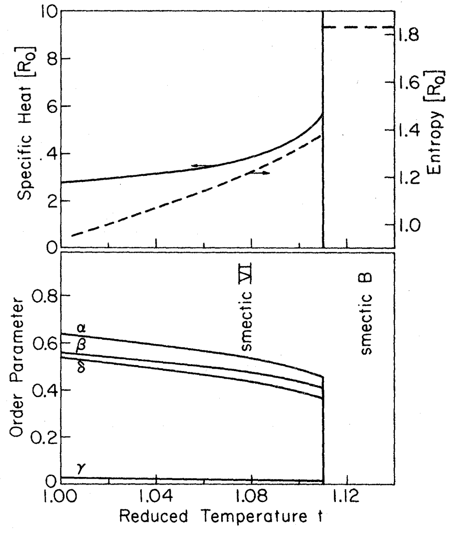

FIG. 8. Order parameters, entropy, and specific heat vs reduced temperature, showing the first-order smectic *B*-VI transition, for $V_1/kT_c^{BH}=4.1$.

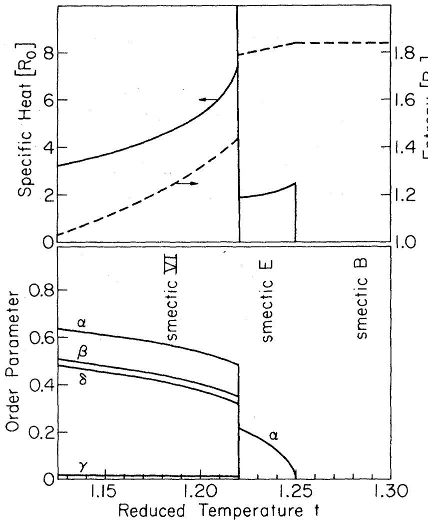

FIG. 9. Order parameters, entropy, and specific heat vs reduced temperature, showing the second-order smectic *B*-*E* and first-order *E*-VI transitions, for $V_1/kT_c^{BH}=5.0$.

which neglects short-range order and the effect of fluctuations of the order parameters. (ii) We have assumed a model of rigid molecules which means, in effect, that we have assumed that the internal motions of the molecules are not affected by phase transitions. (iii) The hard-core part of the exchange interaction has been ignored insofar as it affects the orientation of the molecules.

Assumption (ii) has been shown to be wrong by experiment. We now know that the aliphatic end chains of the molecule show decreasing order as the temperature is raised.[15,16] The ordering of the end chains will increase the entropy changes of the phase transitions. However, the end chains will probably not appreciably effect orientational ordering of the molecules.

A difficulty with the model of the *H* phase[10] is that there is no *a priori* coupling between the tilt direction, or direction of dipole alignment, and the basis vectors of the two-dimensional hexagonal lattice. This difficulty remains in the present treatment in that the slowly varying part of the phenyl-phenyl interaction (we exclude the hard-core part) also does not couple the dipole orientation or tilt direction to the hexagonal lattice. Experimentally, the molecule tilts toward the $\vec{a}$ vector of the lattice.[11] (deVries[31] has correctly pointed out that Fig. 1(e) of the paper of McMillan and the author[10] mistakenly showed the dipoles oriented along the $\vec{b}$ axis of the lattice.) The hard-core term in the exchange interaction [ignored through assumption (iii)] makes it energetically unfavorable for the molecules to tilt along the $\vec{b}$ direction, since the "hard disk" of the rings has a diameter of 6.7Å, while the $\vec{b}$ translation vector has a length of ~5.2Å for TBBA.[11] Thus the hard-core term gives preference to tilt in the $\vec{a}$ direction. For a non-hexagonal lattice the term discussed in Eq. (5b) will couple the tilt to the lattice. This is similar to the "anisotropy field" of the antiferromagnet discussed by Ziman.[32] In the smectic VI phase, the coupling of the dipoles to the lattice occurs naturally. It is more favorable energetically to have tilt along the $\vec{a}$ than the $\vec{b}$ axis, even for a pure hexagonal lattice.

In summary, we have presented a molecular model and shown that, within the mean-field approximation, the model exhibits four phases: smectic *B*, *E*, *H*, and VI phases. The smectic *H* phase is described by two order parameters, $\beta=\langle\cos\phi\rangle$ and $\gamma=\langle\cos2\phi\rangle$. In the smectic *E* phase we have one order parameter $\alpha=\langle-\sin2\phi\rangle$. The smectic VI phase has $\alpha$, $\beta$, $\gamma$, and also $\delta=\langle-\sin\phi\rangle$. The self-consistency equations for these parameters were derived and solved to find the temperature dependence of $\alpha$, $\beta$, $\gamma$, $\delta$, the entropy, and the specific heat. There is not sufficient thermodynamic data presently for comparison to the theory.

## ACKNOWLEDGMENT

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TABLE I. Summary of the description of the phases.

| | | |
|---|---|---|
| Smectic *B* | $\alpha=\beta=\gamma=\delta=0$ | No order on the lattice |
| Smectic *E* | $\beta=\gamma=\delta=0;\ \alpha\neq0$ | Phenyl groups ordered in herringbone pattern |
| Smectic *H* | $\beta\neq0,\ \gamma\neq0,\ \alpha=0,\ \delta=0$ | Angular order of dipoles on lattice |
| Smectic VI | $\alpha\neq0,\ \beta\neq0,\ \gamma\neq0,\ \delta\neq0$ | Dipoles ordered and phenyl groups ordered in herringbone pattern |

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