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Simple molecular theory of the smectic C, B, and H phases

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The molecular theory of the smectic A and C phases is extended to the smectic B and H phases by including a soft-core repulsive interaction in addition to the dipole-dipole interaction used previously. The possibility of translational order (a two-dimensional hexagonal lattice in each smectic plane) is included in addition to the orientational order of the molecular dipoles. Four phases are found: (1) a disordered phase (smectic A), (2) an oriented phase with no translational order (smectic C), (3) a translationally ordered phase with no orientational order (smectic B), and (4) a phase with translational and orientational order (smectic H). In the oriented phases (smectic C and H) the director is tilted with respect to the plane normal. The smectic-A-smectic-C phase transition and the smectic-B-smectic-H phase transition are second order; the other transitions are first order. The temperature dependence of the order parameters, the entropy, and the specific heat are computed.

I. INTRODUCTION

The least ordered of the liquid-crystal phases is the nematic, in which the centers of mass are randomly placed, but the long-axes line up parallel to a preferred axis in space. 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. This model accounts qualitatively for a number of properties of the nematic phase which are inexplicable on the textbook picture; for example, the temperature dependence of the anisotropic dielectric constant and the dielectric relaxation.

The nature of the molecular order in the smectic A phase has been clear for some time. In this phase the long molecular axes lie parallel to an axis in space, the director, and the molecular centers lie on equidistant planes perpendicular to this axis in space. Given the nature of this order Kobayashi[2] and McMillan[3] have been able to formulate microscopic theories of the order. In addition, there is also a Landau theory.[4,5]

In the smectic C phase, the director is tilted with respect to the smectic plane normal, and 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. This orientational order has not yet been confirmed experimentally.

In 1935, Herrmann[8] observed sharp lines in the x-ray powder pattern of a liquid-crystal phase and identified a hexagonal phase. Recent single-crystal x-ray work have confirmed a two-dimensional hexagonal lattice in each smectic plane for the smectic B and H phases, with the director parallel to the plane normal in the smectic B phase and tilted in the smectic H.[9,10]

In this paper, we present a microscopic theory which will include the smectic B and H phases, in addition to the well-understood A and C phases.

We adopt a model in which the smectic A order is well established, the molecules are parallel and sit on planes. The intermolecular potential is taken to be due to (a) dipole-dipole interactions due to permanent dipole moments attached to the molecules and (b) due to a soft-core repulsion between the molecules. We will find that, subject to certain assumptions, we can estimate the order of magnitude of this soft-core repulsion. We examine the phase transitions within the self-consistent-field approximation, neglecting the interplanar interactions and treating only two-dimensional motions of the molecules in one smectic plane. We ignore the question of whether the hexagonal lattices of successive planes are in register. To handle this question, it will be necessary to take interplanar interactions into account, as well as motion of molecular centers away from smectic planes.

The two-dimensional model exhibits three ordered phases in addition to one disordered phase. The transitions vary in order and the phases have different physical properties.

a. Smectic A phase. The phase is characterized by the alignment of the long axis of the molecules along an axis in space and by the ordering of the molecular centers onto planes perpendicular to this axis. Hence this material is optically uniaxial. The molecules are free to move, unordered, in a smectic plane as a two-dimensional liquid [see Fig. 1(b)].

b. Smectic C phase. When the molecular structure is dominated by two outboard oppositely directed dipoles, the first ordered phase occurs. The outboard dipoles on one side of the smectic plane are oriented parallel [see Fig. 2(c)]. The long molecular axis tilts over in the direction of polarization with the tilt angle proportional to $(T_c - T)^{1/2}$. The smectic C phase is optically biaxial, but the optical properties are continuous through the phase transition.

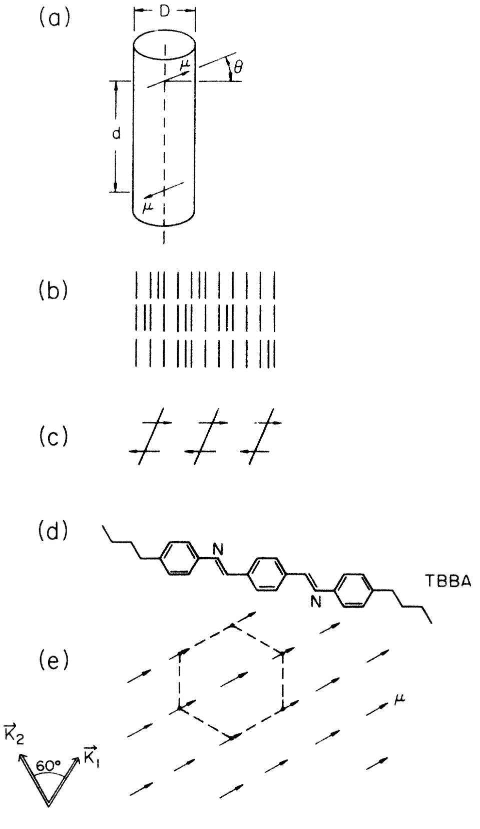

FIG. 1. (a) Molecular model: a cylindrical shape with length L and width D, and two electric dipoles of magnitude μ at a distance $\frac{1}{2}d$ from the center. (b) Molecular order in the smectic A phase. Molecules are free to rotate around the long axis. (c) Molecular order in the smectic C phase with dipoles aligned. (d) The compound terephthal-bis-butyl aniline (TBBA) exhibits a smectic A, C, and H phases. The all-trans-structure is shown. The actual conformations in the liquid-crystal phases are unknown. (e) The hexagonal aligned structure of the smectic H phase. In the smectic B phase the dipoles are unaligned.

c. Smectic B phase. This phase is characterized by a two-dimensional hexagonal order in the smectic plane. The dipole moments are randomly oriented, so the material is optically uniaxial. The molecules are not titled with respect to the normal to the plane.

d. Smectic H phase. This phase is characterized by both two-dimensional hexagonal order and alignment of the dipole moments [see Figs. 1(c) and 1(e)]. Hence the material is optically biaxial. The director will be tilted with respect to the plane normal.

The plan of this paper is as follows. In Sec. II, we will define the model and present the self-consistent equations for the order parameters of the different phases. We will give the energy, entropy, and free energy in terms of the order parameters. We will also derive the temperature of the second-order smectic-B–smectic-H phase transition in terms of the parameters of the model. In Sec. III, we discuss the method of numerical solution of the coupled equations for the order parameters and present the results of these calculations. In Sec.

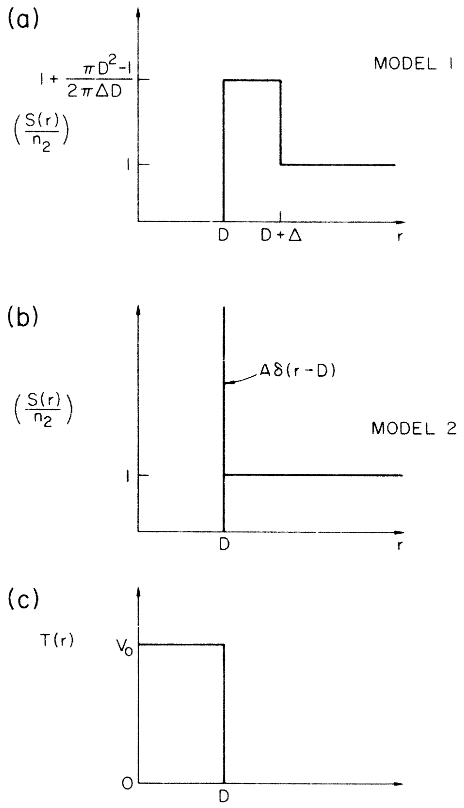

FIG. 2. Two different models for the two-particle correlation function $S(r)$ and the model for the repulsive intermolecular potential $T(r)$.

IV, comparisons will be made with experimental results and subject to certain assumptions; we can infer the magnitude of the repulsive soft-core potential for one organic molecule, terephthal-bis-butylaniline (TBBA). In Sec. V, we will summarize and discuss the shortcomings of the model.

II. THEORETICAL MODEL

We consider one smectic plane in a perfectly ordered smectic *A* phase of a liquid crystal (call it the *xy* plane). In this plane, as is shown in Fig. 1(b), the long rodlike molecules are aligned and have their centers on the plane.

Now consider the model of an organic liquid-crystal-forming molecule proposed by McMillan[7] in his theory of the smectic *C* phase. The molecule is supposed to be as is shown in Fig. 1(a), a long rod with oppositely oriented dipoles titled at an angle θ on opposite sides of the molecular center. This suggests that we assume the following for the form of the two-body interaction between molecules in the plane:

$$U_{12}=\left(\frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r_{12}^3}-\frac{3(\vec{\mu}_1\cdot\vec{r}_{12})(\vec{\mu}_2\cdot\vec{r}_{12})}{r_{12}^5}\right)S(r_{12})+T(r_{12}). \tag{1}$$

If the spacing between dipoles on one molecule d is somewhat larger than the intermolecular spacing a, we may neglect interactions between dipoles on different levels.

The first term in the above potential represents a dipole-dipole interaction, where $S(r_{12})$ is the two-particle correlation function. We have considered two forms for $S(r)$, as shown in Fig. 2. In Fig. 2(a), we have model 1

$$\frac{S(r)}{n_2}=\begin{cases}0, & r<D\\ 1, & r>D+\Delta\\ 1+\dfrac{\pi D^2-1}{2\pi\Delta D}, & D\leq r\leq D+\Delta\end{cases}$$

where n_2 is the particle density in the plane. The function $S(r)$ is chosen to satisfy

$$\int_0^\infty [S(r)-n_2]2\pi r\,dr=-1. \tag{2}$$

In Fig. 2(b), we have model 2, $S(r)=S'(r)+A\delta(r-D)$, where

$$S'(r)=\begin{cases}0, & r<D\\ n_2, & r\geq D\end{cases}$$

and $A=(\pi D^2-1)/2\pi D$ is chosen to satisfy Eq. (2).

The second term in Eq. (1) is a soft-core repulsive potential shown in Fig. 2(c). The magnitude of this repulsive potential, V_0, will be shown to be of fundamental importance in the theory.

It would have been more realistic to have chosen a hard-core repulsive potential with perhaps a van der Waals attractive term. However, such a potential cannot be treated within the framework of the self-consistent-field method and would require more complex mathematical techniques. We regard the soft-core potential as an effective potential which is to be used in conjunction with the self-consistent-field approximation.

Throughout these calculations we have chosen the diameter D of the molecules and the interparticle distance a to be related by $a=D+\epsilon$, where $\epsilon\ll a$ and ϵ is positive.

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_1. The one-particle distribution function is then $f_1=e^{-V_1/kT}$. We then recalculate the averaged potential $\bar{V}_1$ which one molecule feels due to all the other molecules; this potential is averaged over the positions and orientations of the other molecules. Thus, $\bar{V}_1=\int d^2x_2\,d\varphi_2\,U_{12}f_1$. The self-consistency requirement that $V_1=\bar{V}_1$ gives the equations for the order parameters. This is the same methodology that was used in the previous molecular theories of liquid crystals.

In order to include the possibility of translational

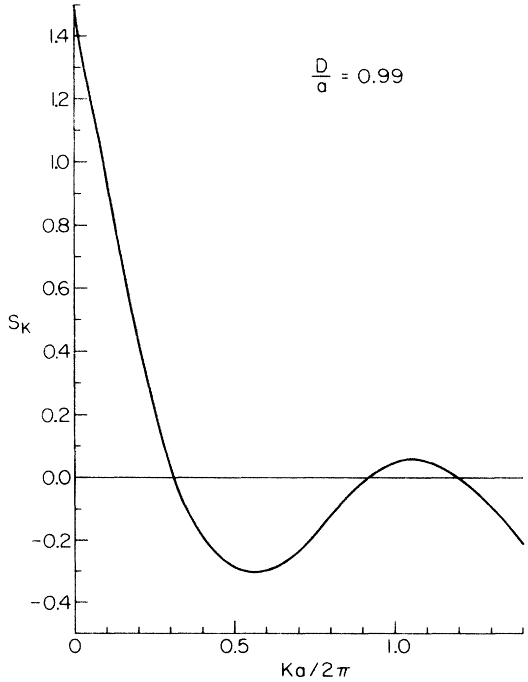

FIG. 3. The function S_K for model 2 with $D=0.99a$. This gives $S_0/S_K=23.1$.

and orientational order and to achieve self-consistency, we choose V_1 to be of the following form:

$$V_1 = +3T_K\alpha(\cos\vec{K}_1\cdot\vec{x}_1+\cos\vec{K}_2\cdot\vec{x}_1+\cos\vec{K}_3\cdot\vec{x}_1) - (\mu^2S_0)\beta\cos\varphi_1 - 3(\mu^2S_K)\gamma\cos\varphi_1 \times(\cos\vec{K}_1\cdot\vec{x}_1+\cos\vec{K}_2\cdot\vec{x}_1+\cos\vec{K}_3\cdot\vec{x}_1). \tag{3}$$

The physical significance of $\bar{K}_1$ and $\bar{K}_2$ are shown in Fig. 1(e). Thus, $\vec{K}_3=\vec{K}_2-\vec{K}_1$. The magnitude of $\vec{K}_1$, $\vec{K}_2$, and $\vec{K}_3$ are given by $|\vec{K}_i|=2\pi/a$. The quantities S_G and T_G (see Figs. 3 and 4, respectively) are related to the zeroth- and first-order terms in the Fourier expansion of the potential U_{12}:

$$S_G = 2\pi\int_0^\infty dr J_0(Gr)S(r)/r^2, \tag{4a}$$

$$T_G = 2\pi\int_0^\infty dr\, r J_0(Gr)T(r). \tag{4b}$$

Throughout this calculation, we ignore all higher Fourier components of the potential.

With the one-particle potential given by Eq. (3), the one-particle distribution function is then

$$f_1(x_1, y_1, \varphi_1) = \exp[-V_1(x_1, y_1, \varphi_1)/kT]. \tag{5}$$

The average of a function A of x, y, and φ is defined by

$$\langle A(x,y,\varphi)\rangle_f = \frac{\int d^2x\int_0^{2\pi}d\varphi\, A(x,y,\varphi)f(x,y,\varphi)}{\int d^2x\int_0^{2\pi}d\varphi\, f(x,y,\varphi)}. \tag{6}$$

Using Eq. (6) and the two-body potential (1), we recalculate the one-body potential

$$\begin{aligned}\bar{V}_1(x_1,y_1,\varphi_1) &= \frac{N\int d^2x_2 d\varphi_2 U_{12}(\vec{r}_{12},\varphi_2)f(\vec{x}_2,\varphi_2)}{\int d^2x_2 d\varphi_2 f(\vec{x}_2,\varphi_2)}\\ &= N[(-\mu^2S_0)\langle\cos\varphi_2\rangle_f\cos\varphi_1 + (-\mu^2S_K)\cos\varphi_1(\cos\vec{K}_1\cdot\vec{x}_1+\cos\vec{K}_2\cdot\vec{x}_1+\cos\vec{K}_3\cdot\vec{x}_1)\\ &\quad\times\langle\cos\varphi_2(\cos\vec{K}_1\cdot\vec{x}_2+\cos\vec{K}_2\cdot\vec{x}_2+\cos\vec{K}_3\cdot\vec{x}_2)\rangle_f + T_K(\cos\vec{K}_1\cdot\vec{x}_1+\cos\vec{K}\cdot\vec{x}_1+\cos\vec{K}_3\cdot\vec{x}_1)\\ &\quad\times\langle\cos\vec{K}_1\cdot\vec{x}_2+\cos\vec{K}_2\cdot\vec{x}_2+\cos\vec{K}_3\cdot\vec{x}_2\rangle].\end{aligned} \tag{7}$$

Self-consistency of (7) and (3) requires

$$\alpha = \tfrac{1}{3}\langle\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x}\rangle_f, \tag{8a}$$

$$\beta = \langle\cos\varphi\rangle_f, \tag{8b}$$

$$\gamma = \tfrac{1}{3}\langle\cos\varphi(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})\rangle_f. \tag{8c}$$

This set of three coupled equations [Eqs. (8)] must be solved self-consistently for the three order parameters α, β, and γ.

The orientational order parameter is β; when β is finite, the dipoles are aligned parallel to an axis lying in the smectic plane. There is no net dipole moment, but it follows from previous arguments that the liquid crystal is biaxial and tilted. With $\beta=0$, the liquid crystal is uniaxial, untilted, and there is no orientational order.

The translational order parameter is α. When α is finite, the molecules sit on a two-dimensional hexagonal lattice in each smectic plane. When $\alpha=0$, the molecules move as a two-dimensional liquid.

The order parameter γ describes the coupling between the translational and orientational order and is finite only when both α and β are finite.

The entropy S of a system of molecules with partition function Q is given by

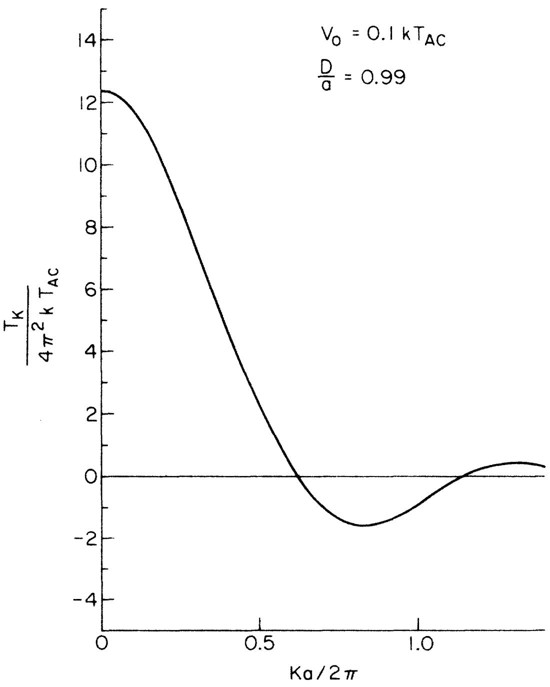

FIG. 4. The function T_K for $D=0.99a$, $V_0=0.1\,kT_{AC}$. The units of T_K are [energy×cm^2].

$$-TS=-kT\ln Q-kT^2\frac{\partial \ln Q}{\partial T}.$$

From this, we easily find

$$-TS=-RT\ln Q+N\left(-9T_K\alpha^2+\mu^2S_0\beta^2+\mu^2S_K9\gamma^2\right). \tag{9}$$

The interval energy is just give by

$$U=\tfrac{1}{2}\left\langle\left\langle\sum_{i,j}U_{ij}\right\rangle_i\right\rangle_j$$

from which we find

$$U=-\tfrac{1}{2}N(\mu^2S_0\beta^2+\mu^2S_K9\gamma^2-T_K9\alpha^2). \tag{10}$$

The free energy is then $F=U-TS$. Equations (8) for the order parameters can be found simply by minimizing the free energy F with respect to the order parameters. In order to determine which of the phases is stable at a given temperature, we must examine the free energy of the system.

Finally, the specific heat is given by

$$C_V=T\frac{\partial S}{\partial T}. \tag{11}$$

Now we have all the equations which we need to calculate the physical properties of the model.

McMillan[7] has solved the model for the temperature of the second-order smectic-A– smectic-C phase transition. In terms of our variables, we find

$$T_{AC}=\mu^2S_0/2k_B. \tag{12}$$

In the rest of this paper, we will often use the reduced temperature $t=T/T_{AC}$.

Now we will solve for the reduced temperature of the second-order smectic-B–smectic-H phase transition. First, define the variables

$$u_0=-3T_K\alpha/Tk_B\,,$$

$$u_1=\mu^2S_0\beta/Tk_B\,,$$

$$u_2=3\mu^2S_K\gamma/Tk_B.$$

Expanding the exponentials in Eqs. (8a)–(8c) and keeping first-order terms in u_1 and u_2 gives

$$tu_1=u_1+u_2f(u_0), \tag{13a}$$

$$Btu_2=u_1f(u_0)+u_2g(u_0), \tag{13b}$$

where

$$f(u_0)=\frac{\int d^2x(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})\exp[u_0(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})]}{\int d^2x\exp[u_0(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})]},$$

$$g(u_0)=\frac{\int d^2x(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})^2\exp[u_0(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})]}{\int d^2x\exp[u_0(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})]},$$

and $B=S_0/S_K$. Solving those equations for the limit u_1, u_2 vanishing gives

$$t_{BH}=1+\frac{f^2(u_0)}{B}+\frac{g^2(u_0)}{4B^2}. \tag{14}$$

At this point a brief discussion of the different models of $S(r)$ is necessary. As we shall see in Sec. III, it is possible to get two different forms for the phase diagram, depending on the sign of B (see Figs. 5 and 6.) For example, in model 1, if we choose $D=0.75a$ and $\Delta=\frac{1}{2}a$, where a is the interparticle distance, we find $B=-20.8$. For $D=0.88a$ and $\Delta=\infty$, we find $B=-35.0$. In model 2 (see Fig. 2), with $D=0.99a$, we find $B=+23.1$. The important factor is that in these models $|B|\gg 1$.

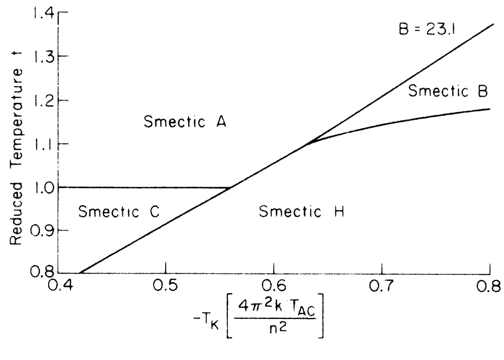

FIG. 5. Phase diagram of the theoretical model showing transition temperature in reduced units (T/T_{AC}) vs $-T_K=8.137\ V_0$ for $B=23.1$.

III. NUMERICAL RESULTS

In this section, we will solve the self-consistent equations [Eqs. 8(a)–8(c)] for the order parameters. As we saw in Sec. II, it is an easy step from there to find the entropy, free energy, energy, and specific heat.

In order to solve Eqs. (8) we must be able to perform the integration over x, y, and φ. To do this, we first expand $f(x,y,\varphi)$ in a power series

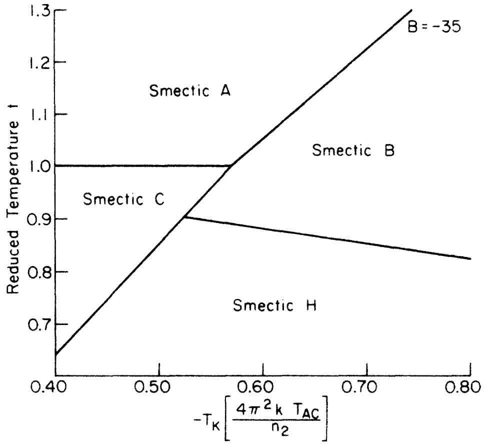

FIG. 6. Phase diagram for $B=-35$, model 1 for $S(r)$.

in α and γ. For the *m*th term, we have

$$(\alpha+\gamma\cos\varphi)^m(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})^m=c_m\,.$$

We expand this term in a Fourier series,

$$C_m=a_0\cdot 1+a_1(\cos\vec{K}_1\cdot\vec{x}+\cos\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x})$$
$$+a_2(\cos 2\vec{K}_1\cdot\vec{x}+\cos 2\vec{K}_2\cdot\vec{x}+\cos\vec{K}_3\cdot\vec{x}2). \quad (15)$$

In Eq. (15), we only want the a_0 coefficient, since all other terms average to zero when integrated over a smectic plane.

The φ integrals can be done exactly in terms of linear combinations of the Bessel functions $I_j(\beta)$ or can be done numerically.

We keep as many terms as necessary to obtain the desired accuracy. For $0.8 \leq t \leq 1.2$, it is necessary to keep terms up to $m=20$ or so, because the terms increase in size up to approxi-

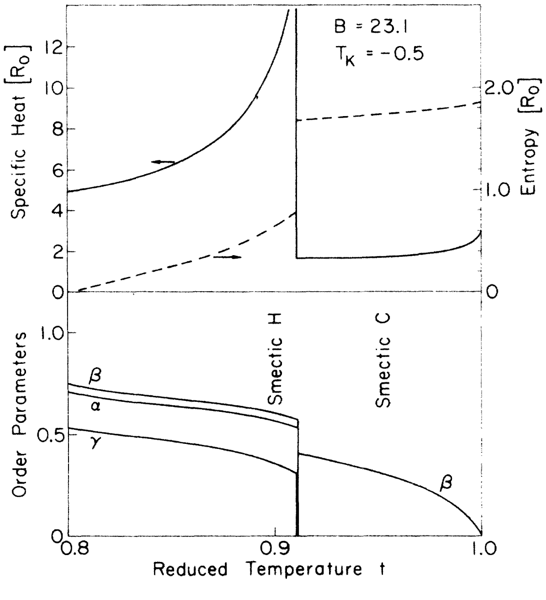

FIG. 7. Order parameters α, β, γ, entropy S, and specific heat C_V vs reduced temperature for the theoretical model with $T_K=-0.5$ showing the second-order smectic-A–smectic-C transition and the first-order smectic-C–smectic-H transition.

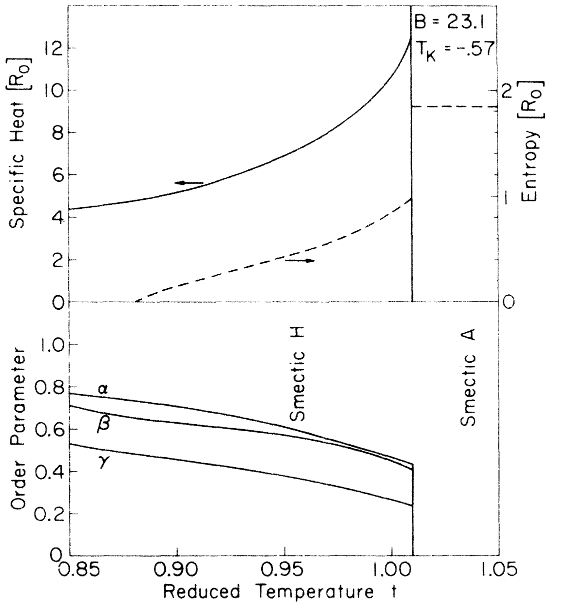

FIG. 8. Order parameters, entropy, and specific heat vs reduced temperature t for $T_K=-0.57$ showing the first-order smectic-A-smectic-H transition.

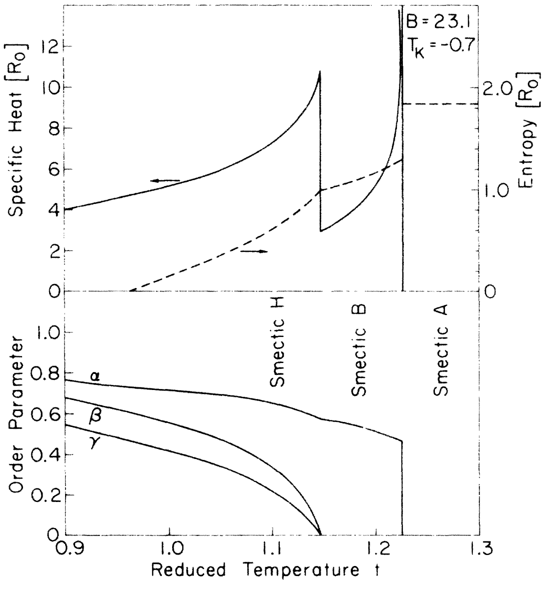

FIG. 9. Order parameters, entropy, and specific heat vs reduced temperature for $T_K=-0.7$ showing the first-order smectic-A–smectic-B transition and the second-order smectic-B–smectic-H transition.

mately $m = 10$ and then decrease.

We will describe how to solve the coupled equations [Eqs. (8)] only for the case of the first-order smectic-*C*-smectic-*H* phase transition, since this is the most difficult. All other cases can be solved by simplifications of this method. First, choose a value of β/t, then, choose trial values of α/t and γ/t, and substitute in Eq. (8b) and determine t. Equation (8a) will not be satisfied, and we must plot $\alpha - \frac{1}{3}\langle\cos\vec{K}_1\cdot\vec{x} + \cos\vec{K}_2\cdot\vec{x} + \cos\vec{K}_3\cdot\vec{x}\rangle_f$ vs α/t to find the best value of α/t. We then do the same for γ/t and Eq. (8c). Iterate until t, $\alpha/t, \beta/t$, and γ/t have reached the desired consistency. Now we must calculate U, F, and S. This calculation is performed at different temperatures and we find C_V from Eq. (11). Near the transition temperature, we must compare the free energy to establish which phase is stable.

The transition temperatures as a function of $-T_K = 8.137V_0$ are shown in the phase diagrams in Figs. 5 and 6 for $B > 0$ and $B < 0$, respectively. The smectic-*A*-smectic-*C* and smectic-*B*-smectic-*H* phase transitions are second order. All other phase transitions are first order. To illustrate these behaviors, we plot in Figs. 7–9 the order parameters, entropy, and specific heat vs t for $B = +23.1$. In each case, the values of T_K are chosen to represent typical phase transitions shown in Fig. 5. In Fig. 10, we plot ΔS as a function of T_K for $B = 23.1$ for the first-order phase transitions. All these phase transitions correspond to the two-dimensional smectic liquid freezing into a two-dimensional hexagonal lattice. We should point out that $\Delta S_{AB} = 0.56R$ is independent of both $B = S_0/S_K$ and T_K. T_K can be related to the height of the repulsive potential by

$$T_K = (2\pi V_0/K)DJ_1(KD). \tag{16}$$

T_K has the units of energy $\times \mathrm{cm}^2$, for the results show in all figures in this paper $T_K = -8.137V_0$. See Table I.

In Sec. IV, we will see we can make predictions of the value of ΔS_{CH} for TBBA [see Fig. 1(d)]. In the course of this, we predict the value of V_0 for TBBA, and these estimates vary only over a few percent as we vary B over a range of factor of 4. We find $T_K \approx -0.5$ or $V_0 \approx 2.35kT_{AC}^{\mathrm{TBBA}} = 0.1$ eV.

TABLE I. Summarization of the description of the phases.

Smectic *A*	$\alpha = \beta = \gamma = 0$	no order in plane
Smectic *B*	$\beta = \gamma = 0, \alpha \neq 0$	translational order in plane
Smectic *C*	$\alpha = \gamma = 0, \beta \neq 0$	angular order of dipoles in plane
Smectic *H*	$\alpha \neq 0, \beta \neq 0, \gamma \neq 0$	angular and translational order in plane

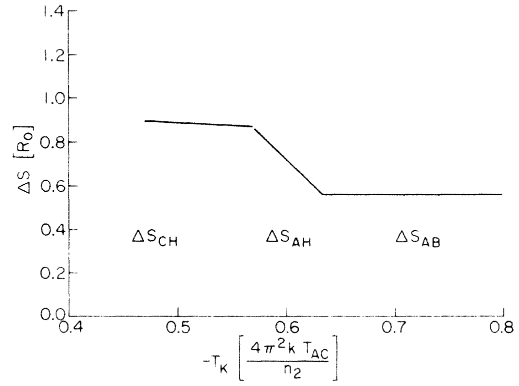

FIG. 10. First-order transition entropy change vs $-T_K$ for $B = 23.1$, model 2 of $S(r)$.

IV. COMPARISON WITH EXPERIMENT

Although there have been extensive studies of liquid-crystal transition entropies, we do not have much data suitable for comparison with our theory. This is due to the fact that the differentiation between smectic *B* and smectic *H* is a comparatively recent one in the literature.[10] We do have some data though.

Arnold and Roediger[11] have data for ethyl-ethoxybenzylidene amino cinnamate (EEBAC) which shows that $\Delta S_{AB}^{\mathrm{EEBAC}} = 0.65\ R_0$. Also, the value for *p*-*n*-octyloxybenzylidene-*p*′-toluidine (OBT) has been measured $\Delta S_{AB}^{\mathrm{OBT}} = 1.0R_0$. This is to be compared with our value, which is independent of all parameters in the model of $\Delta S_{AB} = 0.56R_0$.

For TBBA, we have $\Delta S_{CH}^{\mathrm{TBBA}} = 1.4R_0$. If we assume $B = 23.1$, then we calculate $\Delta S_{CH} = 0.88R_0$. If we assume $B = 100$, then we calculate $\Delta S_{CH} = 0.74R_0$. Unfortunately, we have been unable to devise a way to measure $S_0/S_K = B$ experimentally.

In the cases mentioned above, we note that ΔS^{calc} is invariably less than ΔS^{expt}. This is probably true in general. If internal motions, such as rotations around single bonds, are frozen out of the molecules when they go into the two-dimensional solid phase, then the change in entropy would be larger than calculated. Further, if the smectic *A* order were not perfect, then additional entropy would be added to ΔS_{AH} and ΔS_{AB}. Our theory is at constant volume with a soft-core potential. If we used a hard-core potential, we would find a change of volume at the smectic-*A*-smectic-*B* phase transition. We would also have a larger change of order parameters and larger ΔS.

V. CONCLUSIONS

We have presented a simple molecular model and shown that, within the mean-field approximation, the model exhibits four phases; smectic *A*, *B*, *C*, and *H* phases. The smectic *B* phase is described by a translational order parameter $\alpha = \frac{1}{3}\langle \cos\vec{K}_1\cdot\vec{x} + \cos\vec{K}_2\cdot\vec{x} + \cos\vec{K}_3\cdot\vec{x}\rangle_f$. The smectic *C* phase is described by an orientational order parameter $\beta = \langle \cos\varphi\rangle_f$. In the smectic *H* phase, we have three order parameters; α, β, and $\gamma = \frac{1}{3}\langle \cos\varphi(\cos\vec{K}_1\cdot\vec{x} + \cos\vec{K}_2\cdot\vec{x} + \cos\vec{K}_3\cdot\vec{x})\rangle_f$. The self-consistency equations for these parameters were set up and were solved to find the temperature dependence of α, β, γ, the entropy, and the specific heat. The experimental evidence that we have examined indicates that the theoretical model predicts transition entropies qualitatively and so the model is probably satisfactory for the smectic *B*, *C*, and *H* phases. In the case of the smectic *C* phase this reduces exactly to the theory of McMillan.[7]

The assumed order in the various phases is as follows (assuming rigid molecules):

(i) In the *smectic A* phase, the long-axes line up preferentially parallel to the direction in space; there is free rotation about the long axis; the centers of mass sit preferentially near planes normal to the preferred axis with an interplanar spacing of the order of the molecular length (the one-dimensional density wave); and the centers of mass move randomly in the plane. If the molecules are asymmetric and have a dipole moment, it is assumed that the dipole moments are not aligned.

(ii) When the molecular structure is dominated by the two oppositely directed dipoles, we have the *smectic C* phase. The dipoles on one side of the plane are oriented parallel. The long molecular axis tilts over in the direction of polarization. There is no translational order in the plane.

(iii) When the molecular structure is dominated by the repulsive soft core, we have the *smectic B* phase. The molecules remain free to rotate about the long molecular axis. The two-dimensional liquid has frozen into a two-dimensional hexagonal crystal.

(iv) The phase with the highest order is the *smectic H* phase. The dipoles on each side of the plane orient and the molecular centers are arranged in a two-dimensional hexagonal lattice. The long molecular axis tilts over in the direction of polarization.

It is worthwhile to list some of the assumptions and approximations which we have made. (i) The models for the two-particle-correlation function $S(r)$ have been crude. The actual form lies somewhere between the two models. (ii) The actual form of the potential $T(r)$ is not known, but probably contains a hard core, which cannot be handled by these methods. (iii) We have worked within the mean-field approximation which neglects short-ranged order and the effects of the fluctuations of the order parameters. (iv) 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.

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