PHYSICAL REVIEW A VOLUME 18, NUMBER 3 SEPTEMBER 1978

Molecular ordering in the smectic-E phase in the molecular-field approximation*

J. Felsteiner and D. Cabib
Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel

Z. Friedman
Physics Department, Duke University, Durham, North Carolina 27706

(Received 26 October 1976; revised manuscript received 11 August 1977)

The smectic-B to smectic-E transition is discussed in terms of an orientational intermolecular potential recently suggested by Meyer. Within the framework of the molecular-field approximation the transition temperature is obtained from the lowest eigenvalue of an Hermitian matrix, and the ordered state below it is described by the corresponding eigenvector. A condition is found for which the experimentally observed herringbone structure is the most stable one.

I. INTRODUCTION

The richness of liquid-crystal phases seems so great to the reader of the literature on this subject, that it is not surprising that their understanding is often far from being satisfactory. In some instances different groups of authors disagree as to the characterization and interpretation of these phases, and even to their names. An example is given by those smectic phases which present the highest order, and whose distinction from the solid at lower temperatures is not clearcut. For a brief review of these smectic phases we refer the reader to the paper by de Vries.[1]

X-ray-diffraction experiments[2] have been reported on a series of materials, in which the molecules in the smectic layer occupy the positions of a hexagonal lattice. We will restrict ourselves to the discussion of this particular modification of the smectic phase, leaving out other important ordered smectic phases (e.g., BBEA and TBBA), which are not strictly hexagonal.[3,4]

Doucet *et al.*[2] studied the following materials: *p*-phenyl benzilidene-*p*-amino-*n*-pentyl-cinnamate (PABC), *p*-phenyl-benzilidene-*p*-amino-methyl 2-butyl-cinnamate (PBAMBC*), and *p*-phenyl-benzilidene-*p*-amino-methyl 1-heptyl-cinnamate (PBAMHC*). Each of these three materials has a phase diagram of the following sort[2]:

$$\text{solid} \rightleftarrows \text{smectic } E \rightleftarrows \text{smectic } B$$

$$\rightleftarrows \text{smectic } A \rightleftarrows \text{isotropic liquid.}$$

The smectic-A modification[5] is characterized by the parallel arrangements of the long molecular axes (as in the nematic phase) and by the ordering of the molecules in parallel layers, perpendicular to the direction of the nematic order. In the smectic-B phase the appearance of order within the layer is observed[2]: the molecular centers form a hexagonal lattice in two dimensions but there is no order between layers. The short molecular axes are not ordered and therefore the molecules can rotate around their long axis, in this phase. These facts seem to be well established experimentally, even though the question of the molecular rotation in similar phases (e.g., the H phase of TBBA) is a subject of controversy.[1,6] For a classification of B phases see also Ref. 7.

The x-ray experiments on "monodomains" show[2] the existence of a different smectic phase, at temperatures below 160 or 168 ℃ (according to the material) which is obtained by cooling the smectic B. This phase is called smectic E, and the x-ray data are interpreted[2] by assuming a freezing of the molecular rotational degree of freedom around the long axis. A small orthorhombic distortion of the lattice is also observed[2] at this B-E phase transition.

The purpose of the present paper is to show how the nature of the ordered E phase can be obtained within the framework of the molecular-field approximation, provided that the orientational intermolecular interaction is known. An estimate of the transition temperature will also be given in terms of the interaction parameters. We assume that in the "disordered" smectic-B phase the centers of the molecules form a rigid two-dimensional hexagonal lattice and that the short molecular axes rotate freely about their long axes which are fixed in a direction perpendicular to the smectic layers. The interaction between layers is neglected, which may be a good approximation for smectic phases, although some three-dimensional order seems to be present in the E phase.[2] We believe that the inclusion of an interlayer interaction should be too small to affect the results, because of the large interlayer distance, as far as the two-dimensional order is concerned; it could, of course, introduce an ordering between the layers and must be taken into account in a calculation of the solid phase.

II. MOLECULAR-FIELD APPROXIMATION

A Landau theory of the B-E phase transition has been presented recently.[8] As usual in such mean-field theories a free-energy functional is written as a function of the order parameter (describing the packing of the molecules in the lower E phase) and then minimized to find its equilibrium value. A similar approach, often in use,[8] is to assume a phenomenological two-body potential $V(\vec{r}_1,\vec{r}_2)$ and an average potential $\overline{V}(\vec{r}_1)$ (dependent upon the order parameter) to which each particle is subjected ($\vec{r}_i$ is the set of degrees of freedom of particle i). The order parameter is then calculated self-consistently imposing the condition

$$\overline{V}(\vec{r}_1)=\int f(\vec{r}_2)V(\vec{r}_1,\vec{r}_2)\,d\vec{r}_2\,, \tag{1}$$

where

$$f(\vec{r}_2)=Ae^{-\overline{V}(\vec{r}_2)/kT} \tag{2}$$

is the (normalized) one-particle distribution function.

In these approximations one has to assume from the beginning the structure of the lower temperature phase in order to define the order parameter and the one-particle potential. There is always the need for a search of the state which stabilizes the free energy (or the energy, at zero temperature), even within a mean-field theory.

In the present work, the hindering of the free rotation of the short molecular axes is assumed to be due to a two-body nearest-neighbor interaction of the form[8]

$$\begin{aligned}V_{ij}(\phi_i,\phi_j,\xi_{ij})=&A\cos^2(\phi_i-\phi_j)\\&+B\cos(4\xi_{ij})\cos2(\phi_i+\phi_j)\\&+B\sin(4\xi_{ij})\sin2(\phi_i+\phi_j)\,.\end{aligned} \tag{3}$$

The definition of ϕ_i, ϕ_j, and ξ_{ij} is given in Fig. 1. Equation (3) is the simplest interaction potential compatible with the symmetry of the lattice. Any realistic interaction, which might include quadrupole-quadrupole, Van der Waals, and exchange terms (the exchange term being approximated as in Meyer[8]), will have a form similar to this.

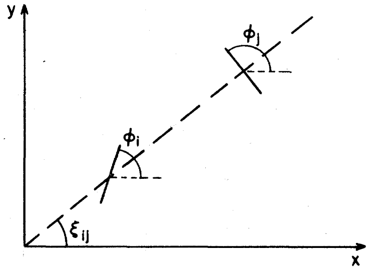

FIG. 1. Definition of the angles ϕ_i, ϕ_j, and ξ_{ij} in the notation of Meyer (Ref. 8). The x axis is in the direction of a primitive hexagonal lattice vector. The xy plane is parallel to the smectic layer.

(3) can also be written

$$\begin{aligned}V_{ij}=&[\tfrac{1}{2}A-B\cos(4\xi_{ij})]\sin(2\phi_i)\sin(2\phi_j)\\&+[\tfrac{1}{2}A+B\cos(4\xi_{ij})]\cos(2\phi_i)\cos(2\phi_j)\\&+B\sin(4\xi_{ij})[\sin(2\phi_i)\cos(2\phi_j)\\&\qquad+\cos(2\phi_i)\sin(2\phi_j)]\,.\end{aligned} \tag{4}$$

The orientational potential is thus given by

$$V=\frac{1}{2}\sum_{ij}V_{ij}\,, \tag{5}$$

where

$$V_{ij}=\sum_{\mu,\nu=1,2}v_{\mu\nu}^{ij}q_\mu^i q_\nu^j\,,$$

with

$$q_1^i\equiv\sin(2\phi_i),\quad q_2^i\equiv\cos(2\phi_i)\,.$$

Using the abbreviation $s\equiv(i,\mu)$; $t\equiv(j,\nu)$; $r\equiv(j',\nu')$ and the property $v_{\mu\nu}^{ij}=v_{\nu\mu}^{ji}$, we write Eq. (5) as

$$\begin{aligned}V=&\frac{1}{2}\sum_{ts}v_{ts}q_tq_s\\&\approx\sum_{ts}v_{ts}\langle q_t\rangle q_s+\text{const}\,,\end{aligned} \tag{6}$$

where (6) is the mean-field approximation. Then the thermal average of q_r is given by

$$\begin{aligned}\langle q_r\rangle=&\int\cdots\int_0^{2\pi}q_r\exp\Big(-\beta\sum_{ts}v_{ts}\langle q_t\rangle q_s\Big)d\phi_1\cdots d\phi_N\\&\times\Big[\int\cdots\int_0^{2\pi}\exp\Big(-\beta\sum_{ts}v_{ts}\langle q_t\rangle q_s\Big)d\phi_1\cdots d\phi_N\Big]^{-1}\,,\end{aligned} \tag{7}$$

where N is the total number of molecules in a smectic layer and $\beta=1/kT$.

Expanding the exponents to terms linear in q_s, and noting that

$$\int_0^{2\pi}q_\mu^i\,d\phi_i=0\,,\quad\int_0^{2\pi}q_\mu^iq_\nu^j\,d\phi_i\,d\phi_j=\tfrac{1}{2}\delta_{ij}\delta_{\mu\nu}\,,$$

we find

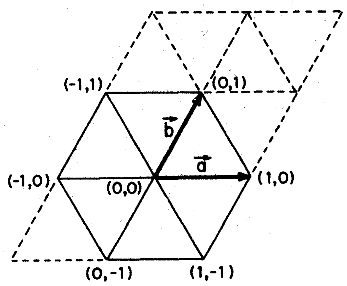

FIG. 2. $\vec{a}$ and $\vec{b}$ are primitive lattice vectors. The coordinates of the nearest neighbors of the site at the origin are also given.

$$\langle q_r\rangle = -\tfrac{1}{2}\beta\sum_t v_{tr}\langle q_t\rangle . \tag{8}$$

Equation (8) is a set of linear homogeneous equations which have a nontrivial solution whenever

$$\det(v_{tr} + 2kT\delta_{tr}) = 0 . \tag{9}$$

The highest T for which the secular equation (9) is satisfied will give an estimate of T_c. Thus, if $\lambda_{\min}$ is the lowest eigenvalue of the interaction matrix v_{tr} the transition temperature T_c is given by

$$kT_c = -\tfrac{1}{2}\lambda_{\min} . \tag{10}$$

(T_c is greater than 0 only if $\lambda_{\min} < 0$.) The corresponding eigenvector gives the ordered structure below T_c. This procedure requires the diagonalization of the matrix v_{tr} both on the site indices i, j and on the indices μ, ν. Noting that the matrix v_{tr} is periodic in space and that it connects every site only with its six nearest neighbors, it is natural and easier to perform first the site diagonalization by means of a Fourier transformation, and then the diagonalization on μ and ν.[9,10]

The Fourier transform of $v^{ij}_{\mu\nu}$ is written

$$v^{\vec{k}}_{\mu\nu} = \sum_{\vec{\tau}} e^{i\vec{k}\cdot\vec{\tau}} v^{\vec{\tau}}_{\mu\nu} , \tag{11}$$

where the sum is performed over the six vectors $\vec{\tau}$ connecting site i to its neighbors.

We note that the lattice is generated from the two primitive noncolinear vectors $\vec{a}$ and $\vec{b}$ described in Fig. 2. Let $\vec{k}$ be given by $\vec{k} = 2\pi k_1\vec{a}^* + 2\pi k_2\vec{b}^*$, where $\vec{a}^*$ and $\vec{b}^*$ are the primitive reciprocal-lattice vectors:

$$a^* = (1/a, -1/a\sqrt{3}, 0) , \tag{12}$$

$$b^* = (0, 2/a\sqrt{3}, 0) . \tag{13}$$

In Eq. (11), $\vec{\tau}$ assumes the six values $\pm\vec{a}$, $\pm\vec{b}$, and $\pm(\vec{b}-\vec{a})$. In each case the scalar product $\vec{k}\cdot\vec{\tau}$ is

$$\vec{k}\cdot\vec{a} = 2\pi k_1 , \tag{14a}$$

$$\vec{k}\cdot\vec{b} = 2\pi k_2 , \tag{14b}$$

$$\vec{k}\cdot(\vec{a}-\vec{b}) = 2\pi(k_1 - k_2) . \tag{14c}$$

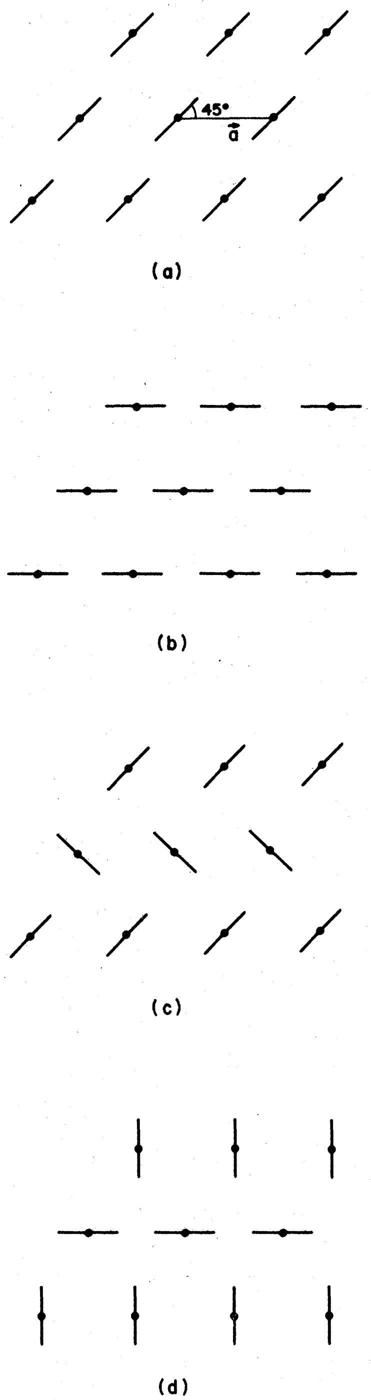

FIG. 3. Structures of lowest energy. The molecules are seen from a direction perpendicular to the smectic layer. The dots are the lattice sites, the lines are the short molecular axes. (a) $\vec{k} = (0,0)$ with $\lambda_1 = 3A$; (b) $\vec{k} = (0,0)$, $\lambda_1 = 3A$; (c) $\vec{k} = (0,\frac{1}{2})$, $\lambda_1 = -A - 4B$; (d) $\vec{k} = (0,\frac{1}{2})$, $\lambda_1 = -A + 4B$. In cases (a) and (c) the angle between the short molecular axis and the x axis is ± 45°, in cases (b) and (d) it is 0° or 90°. [The structures for $\vec{k} = (\frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2})$ can be obtained by ± 60° rotation of $\vec{k} = (0, \frac{1}{2})$ and have the same eigenvalues.]

Substituting Eq. (14a-c) into Eq. (11) we obtain

$$v^{\vec{k}}_{\mu\nu}=\begin{pmatrix} A\gamma_A(\vec{k})-2B\gamma_B(\vec{k}) & B\gamma_C(\vec{k}) \\ B\gamma_C(\vec{k}) & A\gamma_A(\vec{k})+2B\gamma_B(\vec{k}) \end{pmatrix}, \tag{15}$$

where

$$\gamma_A(\vec{k})=\cos(2\pi k_1)+\cos(2\pi k_2)+\cos 2\pi(k_1-k_2),$$
$$\gamma_B(\vec{k})=\cos(2\pi k_1)-\tfrac{1}{2}\cos(2\pi k_2)-\tfrac{1}{2}\cos 2\pi(k_1-k_2), \tag{16}$$
$$\gamma_C(\vec{k})=\sqrt{3}\,[\cos 2\pi(k_1-k_2)-\cos 2\pi k_2].$$

The diagonalization of $v^{ij}_{\mu\nu}$ will be completed by diagonalizing (15).

The eigenvalues of (15) are

$$\lambda_1(\vec{k})=A\gamma_A-|B|\gamma_D,\quad \lambda_2(\vec{k})=A\gamma_A+|B|\gamma_D, \tag{17}$$

where

$$\gamma_D=(4\gamma_B^2+\gamma_C^2)^{1/2}. \tag{18}$$

It is the lower eigenvalue λ_1 that is of interest. The corresponding eigenvector is

$$\begin{pmatrix}\sin\eta\\ \cos\eta\end{pmatrix}, \tag{19}$$

where

$$\tan\eta=\frac{B\gamma_C}{2B\gamma_B+|B|\gamma_D}=\frac{2B\gamma_B-|B|\gamma_D}{B\gamma_C}; \tag{20}$$

when γ_C vanishes the expression that is not indeterminate should be used. The structure below the phase transition is determined by this eigenvector:

$$\langle\sin 2\phi_i\rangle=\langle q_1^i\rangle=\sin\eta\exp(-i\vec{k}\cdot\vec{r}_i),$$
$$\langle\cos 2\phi_i\rangle=\langle q_2^i\rangle=\cos\eta\exp(-i\vec{k}\cdot\vec{r}_i). \tag{21}$$

The ordered state of the system is described by the eigenvector that corresponds to the lowest eigenvalue which in turn depends on the values of the interaction parameters A and B.

III. CONCLUSIONS

For given values of A and B, one method of proceeding would be to cover the first Brillouin zone with a suitably close-spaced grid (e.g., $k_1=n_1/2000$, $k_2=n_2/2000$, where n_1 and n_2 are integers ranging from 0 to 1999), and perform a computer search for the minimum eigenvalue. This is in some respects equivalent to assuming the ordered phase forms a periodic array up to a certain maximum periodicity and checking the obvious cases; however, the difference is that we have checked 4×10^6 cases and can easily verify that no more complicated array need be considered, since the γ's and λ_1 are smooth functions of $\vec{k}$. Thus the method has significant generality.

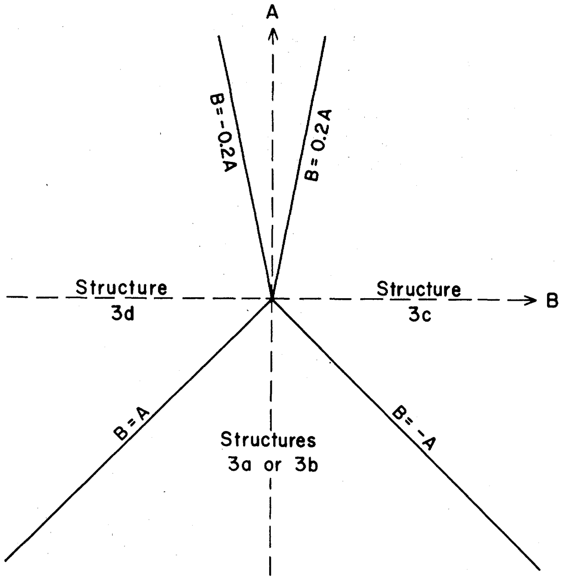

FIG. 4. Diagram of the boundaries between the lowest energy structures. A and B are the interaction parameters.

We have made a search through $\vec{k}$ space and have found the minimum eigenvalue as a function of A and B. The corresponding structures and their boundaries are shown in Figs. 3 and 4, respectively. It is to be noted that the structure does not change abruptly as B changes sign but in fact there is a continuous change in $\vec{k}$ from structure 3c to structure 3d between the lines $B=0.2A$ and $B=-0.2A$, when A is positive.

Taking the estimated values of V_0 and V_1 for TBBA from Meyer's work,[11] we obtain: $A=0.67\times10^{-13}$ erg and $B=1.0\times10^{-13}$ erg (for the definition of V_0 and V_1 see Meyer's paper[8]). The minimum eigenvalue for this choice of A and B is $\lambda_1=-(A+4B)$, which occurs for $k_1=0$ and $k_2=\frac{1}{2}$. This corresponds to the herringbone structure 3c, and is the structure which has been observed experimentally.[2]

---

*Supported in part by the Israel Commission for Basic Research.

[1] A. de Vries, J. Phys. (Paris) 36, C1-1 (1975).

[2] J. Doucet, A. M. Levelut, M. Lambert, L. Liebert, and L. Strzelecki, J. Phys. (Paris) 36, C1-13 (1975).

[3] A. de Vries and D. Fishel, Mol. Cryst. Liquid Cryst. 16, 311 (1972).

[4] A. de Vries, J. Chem. Phys. 61, 2367 (1974).

[5] P. G. de Gennes, ***The Physics of Liquid Crystals*** (Clarendon, Oxford, 1974).

[6] J. Doucet, A. M. Levelut, and M. Lambert, Phys. Rev. Lett. 32, 301 (1974).

[7] A. de Vries, Chem. Phys. Lett. 28, 252 (1974).

[8] R. J. Meyer, Phys. Rev. A 13, 1613 (1976).

[9] J. Felsteiner and Z. Friedman, Phys. Rev. B 8, 3996 (1973).

[10] Z. Friedman and J. Felsteiner, Philos. Mag. 29, 957 (1974).

[11] R. J. Meyer, Phys. Rev. A 12, 1066 (1975).