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Orientational ordering and chiral symmetry breaking in organic monolayers composed of disklike mesogenic molecules: Molecular theory and computer simulations

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Orientational ordering of disklike molecules on a flat surface is investigated using a molecular-statistical theory and Monte-Carlo simulations. The theory is based on the two-dimensional orientational order parameter for molecules with a threefold symmetry axis, and on a simple model interaction potential which has been derived taking into consideration only the symmetry of basic molecular structure. The theory reveals three different anisotropic phases. One of them exactly corresponds to the structure which has recently been observed experimentally in self-assembling monolayers of discotic mesogenic molecules on a pyrolitic graphite surface. This is a two-dimensional (2D) chiral anisotropic phase composed of nonchiral molecules. The phase consists of three sublattices with different orientational order. One sublattice is orientationally disordered, while the other two sublattices are ordered with the same scalar order parameter and different orientations of the ordering tensor. Both order parameters of the directions of ordering are determined self-consistently by minimizing the total free energy of the system. The detailed structure of this unusual phase is also confirmed by the results of Monte Carlo simulations based on the same model interaction potential. The results of the theory qualitatively explain existing experimental data and also shed some light on the origin of supramolecular structures observed in 3D columnar phases composed of similar molecules.

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I. INTRODUCTION

Conventional thermotropic liquid crystals are usually composed of rodlike or disklike molecules which can form a large variety of different phases with orientational and, partially, translational order. The simplest liquid crystalline phase is the nematic phase which exhibits only orientational order of the primary molecular axes. Many rodlike mesogenic molecules also form smectic phases which are characterized by one-, two- or even three-dimensional positional order. In such mesophases, the rodlike molecules are packed in layers. Disk-shaped molecules, which normally have planar rigid cores and flexible chain tails, also form nematic phases as well as columnar phases [1], where the molecular cores stack into columns. The most commonly observed columnar phases consist of triangular or rectangular arrays of columns with short-range fluidlike order inside each column [2,3]. There exist also highly ordered columnar phases which are similar to higher smectic phases and to three-dimensional plastic crystals [4]. As discussed by Boden [3] and Guillon [5], the columns are formed due to an attraction between the flat aromatic cores of the disklike molecules while the fluidity of the phase is determined by the long flexible chains attached to the core. In highly ordered phases, this fluidity appears to be strongly restricted. It is interesting to note that the strong repulsion between sufficiently long flexible chains may result in a rather complex structure of some columnar mesophases. This structure may include several different superlattices and spontaneous helical ordering inside the columns [6,7].

At the same time little is known about two-dimensional (2D) ordered phases which may be formed by disklike molecules on a surface. Such molecules have been observed to form self-assembled monolayers at a liquid-solid interface [8,9]. In such monolayers, the molecular disks are parallel to the surface and thus there are no columns. In this case, the particular point symmetry of the molecule is expected to be more important for the phase formation and, in general, the molecule cannot be approximated just by an isotropic disk. Instead, the existence of a threefold symmetry axis which is normal to the molecular core should explicitly be taken into account. In particular, such molecules should exhibit 2D analog of the nematic phase, but with a threefold symmetry axis perpendicular to the surface. In general, such spontaneously ordered 2D systems provide us with important models for new molecularly designed materials with nanoscale structure [10].

Recently, interesting anisotropic phases have been observed in self-assembled monolayers formed by a series of discotic mesogenic molecules on a pyrolithic graphite surface [11]. The corresponding disklike molecules used in the experiment are symmetrically alkoxy-substituted triphenylenes which possess a threefold symmetry axis perpendicular to the flat core. Using scanning tunneling microscopy, Charra and Cousty have observed the emergence of a spontaneously chiral anisotropic phase when increasing the triangular aspect ratio of the molecules which is determined by the alkoxy chain length. The schematic structure of this 2D chiral phase, composed of nonchiral tripod molecules, is presented in Fig. 1 (Structure B). In this phase, the molecular centers are located on the sites of a hexagonal lattice but, at the same time, the molecules form three inequivalent super-

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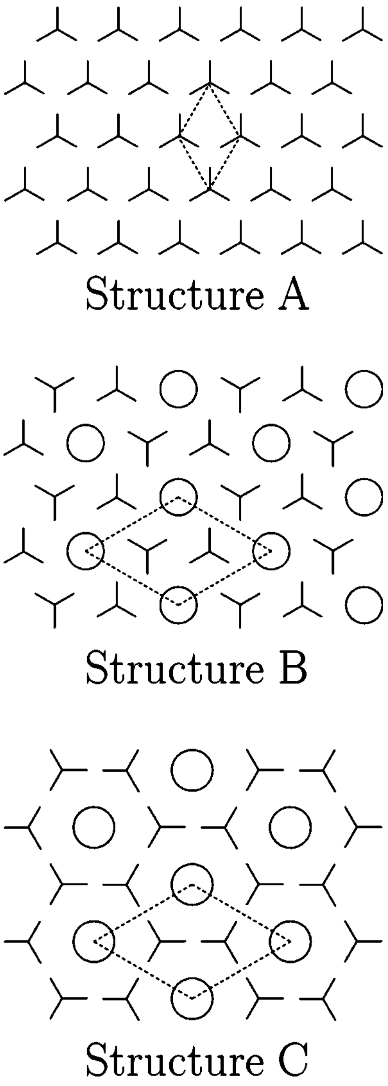

FIG. 1. Three distinct orientationally ordered structures formed by tripod molecules located on the sites of a hexagonal lattice. The unit cell is marked by dashed lines. Structure *A*: homogeneous configuration. Structure *B*: 2D chiral configuration which corresponds to the structure observed by Charra and Cousty. Structure *C*: frustrated honeycomblike structure.

lattices which differ in their orientational order. One superlattice is orientationally disordered while the two others are highly ordered, with antiparallel orientation of the nearest neighbors. The 2D chirality of this phase (see Ref. [12] for a more detailed discussion of 2D chiral systems) is determined by the fact that the ordering directions in two superlattices are not parallel to the axes of the underlying hexagonal lattice formed by molecular centers of mass. These experimental results raise a number of interesting questions about the particular intermolecular interactions which may be responsible for the formation of 2D chiral phases composed of nonchiral molecules. Recently, these effects have attracted significant attention, and a number of chiral textures have been observed in liquid crystal films [13–15] and Langmuir monolayers [16–18].

At present, there is no theoretical description of the new 2D chiral anisotropic phase observed by Charra and Cousty [11] except for some qualitative analogies with frustrated triangular Ising nets [11,19]. There exists also an analogy with the 2D nematic ordering. It should be noted, however, that the triangular (“tripod”) phases presented in Fig. 1 should be characterized by an order parameter, which is a symmetric third-rank tensor (as proposed by Hess [20] for tetratic fluids), while nematics are described by a second-rank tensor order parameter [21]. In this paper, we investigate the ordering of tripod molecules on a surface using a molecular-statistical theory and computer simulations. We show that the relatively complex 2D chiral phase observed by Charra and Cousty [11] can be found both in Monte Carlo simulations and in a mean-field statistical theory, employing a simple and rather general model interaction potential between nonchiral molecules which can be derived taking into consideration only the symmetry of the basic molecular structure. We also compare the transition temperatures and the temperature variation of the order parameters for different superlattices, as obtained from the molecular theory, with the results of the computer simulations.

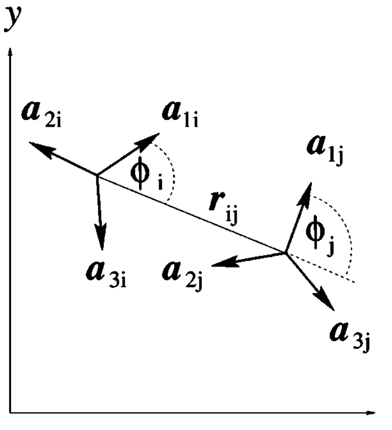

FIG. 2. Coordinates used in modeling the interaction potential between a pair of tripod molecules.

The paper is arranged as follows. In Sec. II, the structure of the orientationally ordered phases formed by tripod molecules on a hexagonal lattice is considered and expressions for the corresponding tensor order parameter are derived. In Sec. III, we derive a model potential of the interaction between tripod molecules with threefold symmetry axes. This model potential is then used in Monte Carlo simulations of the three distinct tripod phases. In Sec. IV, a mean-field theory is developed which describes the transition from the isotropic to the orientationally ordered tripod phase, taking into consideration the spontaneous formation of three inequivalent superlattices accompanied by spontaneous chiral symmetry breaking. The results of this theory are compared with the simulation data In Sec. V, the expression for the chiral order parameter for the orientationally ordered tripod phase is derived and discussed. Some concluding remarks including a discussion of the existing experimental data are presented in Sec. VI.

II. ORDER PARAMETER OF THE TRIPOD PHASE

In this section, we derive an expression for the tensor and scalar order parameters of a 2D orientationally ordered phase composed of triangular (tripod) molecules. Such a molecule is schematically represented in Fig. 2. It has three equivalent chains and possesses a threefold symmetry axis perpendicular to the molecular plane. The homogeneous anisotropic 2D phase composed of such molecules also possesses a threefold symmetry axis and is characterized by three equivalent macroscopic directions within the plane, which make an angle of 120° with each other. It is interesting to compare the symmetry of this new tripod phase with that of the familiar 2D nematic phase composed of rodlike molecules. The 2D nematic phase is characterized by the twofold symmetry axis and as a result there exists only one nonpolar macroscopic direction. By contrast, in the 2D tripod phase all three macroscopic directions are polar.

Now it is possible to derive an expression for the order parameter of the tripod phase using this weak analogy with the 2D nematic phase. The nematic phase is described by the tensor order parameter

$$Q_{\alpha\beta}=S\left(n_\alpha n_\beta-\frac{1}{3}\delta_{\alpha\beta}\right), \tag{1}$$

where S is the scalar order parameter which characterizes the degree of ordering and $\mathbf{n}$ is the unit-vector director which specifies the (nonpolar) direction of ordering. The order parameter $Q_{\alpha\beta}$ is a symmetric and traceless tensor, and Eq. (1) is valid only for the three dimensions, nematic phase as in 3D $\mathrm{Tr}\delta_{\alpha\beta}=3$. In the 2D nematic phase, the tensor order parameter is proportional to $n_\alpha n_\beta-\frac{1}{2}\delta_{\alpha\beta}$ because $\mathrm{Tr}\delta_{\alpha\beta}=2$.

In Eq. (1), the scalar order parameter S is defined as the following ensemble average:

$$S_{3\mathrm{D}}=\langle P_2(\cos\Theta)\rangle, \tag{2}$$

where $P_2(x)$ is the second Legendre polynomial and $\cos\Theta=(\mathbf{a}\cdot\mathbf{n})$ where the unit vector $\mathbf{a}$ is in the direction of the primary molecular axis. In the 2D nematic phase, the definition of S is different because instead of Legendre polynomials one uses the ordinary Fourier expansion. As a result,

$$S_{2\mathrm{D}}=\langle\cos 2\Theta\rangle. \tag{3}$$

Finally, the tensor order parameter $Q_{\alpha\beta}$ can be written as the following average:

$$Q_{\alpha\beta}=\left\langle a_\alpha a_\beta-\frac{1}{D}\delta_{\alpha\beta}\right\rangle, \tag{4}$$

where $D=3$ for the 3D nematic phase and $D=2$ for the 2D one.

One notes that the orientation of a nonpolar rodlike molecule can be specified by the second-rank tensor $a_\alpha a_\beta$ which determines the form of the tensor order parameters (1) and (4). The orientation of a symmetric tripod molecule can be characterized by a symmetric third-rank tensor which depends on the unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ in the direction of the first, second, and third molecular "legs," respectively (see Fig. 2). This tensor can be written as

$$t_{\alpha\beta\gamma}=\overline{a_{1\alpha}a_{2\beta}a_{3\gamma}}, \tag{5}$$

$\alpha,\beta,\gamma=x,y$ and the bar denote the normalized sum over all possible permutations of the indices 1,2,3 because the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are equivalent. One notes also that the unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are related to each other because the molecule is assumed to be rigid. Then the tensor $t_{\alpha\beta\gamma}$ can be expressed in terms of a single unit vector $\mathbf{a}$ taken arbitrarily from the set $(\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3)$. It can be shown after some algebra that the tensor $t_{\alpha\beta\gamma}$ can be expressed as

$$t_{\alpha\beta\gamma}=a_\alpha a_\beta a_\gamma-\tfrac{1}{4}(a_\alpha\delta_{\beta\gamma}+a_\beta\delta_{\alpha\gamma}+a_\gamma\delta_{\alpha\beta}), \tag{6}$$

where the unit vector $\mathbf{a}$ is in the direction of a side chain of the symmetric tripod molecule.

The tensor $t_{\alpha\beta\gamma}$, which characterizes the orientation of a tripod molecule, is analogous to the tensor $a_\alpha a_\beta-\frac{1}{2}\delta_{\alpha\beta}$ for a rodlike molecule. Thus, using this analogy, we can define the macroscopic tensor order parameter of the tripod phase as

$$T_{\alpha\beta\gamma}=\langle a_\alpha a_\beta a_\gamma-\tfrac{1}{4}(a_\alpha\delta_{\beta\gamma}+a_\beta\delta_{\alpha\gamma}+a_\gamma\delta_{\alpha\beta})\rangle. \tag{7}$$

The averaging in Eq. (7) can be performed explicitly using the symmetry of the anisotropic tripod phase and without employing any particular microscopic model. Indeed, Eq. (7) can be rewritten as

$$T_{\alpha\beta\gamma}=\int t_{\alpha\beta\gamma}f_1(\psi)d\psi, \tag{8}$$

where $f_1(\psi)$ is the orientational distribution function of the tripod phase and the angle ψ specifies the orientation of the tripod molecule. As mentioned above, the anisotropic 2D phase composed of tripod molecules possesses a threefold symmetry axis. Therefore, the orientational distribution function of such phase should depend on $\cos 3\psi$, where ψ is the angle between the unit vector $\mathbf{a}$ and a macroscopic director $\mathbf{l}$ [chosen from the set of three equivalent directors $(\mathbf{l}_1\mathbf{l}_2\mathbf{l}_3)$ which make an angle of $2\pi/3$ between each other].

The tensor $t_{\alpha\beta\gamma}$ in Eq. (8) depends on the components a_α [see Eq. (6)] which can be expressed as

$$a_\alpha=n_\alpha\cos\psi+m_\alpha\sin\psi, \tag{9}$$

where the unit vector $\mathbf{m}\perp\mathbf{n}$. Substituting Eq. (9) into Eq. (6) and then into Eq. (8), one obtains

$$T_{\alpha\beta\gamma}=n_\alpha n_\beta n_\gamma\langle\cos^3\psi\rangle+(n_\alpha m_\beta m_\gamma+n_\beta m_\alpha m_\gamma+n_\gamma m_\alpha m_\beta)\times\langle\cos\psi\sin^2\psi\rangle, \tag{10}$$

where we have taken into account that the average of any odd function of ψ vanishes, because the distribution function $f_1(\cos 3\psi)$ is even in ψ.

In Eq. (10), the components of the unit vector $\mathbf{m}$ can be directly expressed in terms of $\mathbf{n}$ taking into account the following relation which is valid in the 2D geometry for any two orthogonal unit vectors $\mathbf{n}$ and $\mathbf{m}$,

$$n_\alpha n_\beta+m_\alpha m_\beta=\delta_{\alpha\beta}. \tag{11}$$

Substituting $m_\alpha m_\beta = \delta_{\alpha\beta} - n_\alpha n_\beta$ into Eq. (10) one obtains, after some straightforward algebra, the following expression for the tensor order parameter of the tripod phase:

$$T_{\alpha\beta\gamma} = \langle \cos 3\psi \rangle \left[n_\alpha n_\beta n_\gamma - \frac{1}{4}(n_\alpha \delta_{\beta\gamma} + n_\beta \delta_{\alpha\gamma} + n_\gamma \delta_{\alpha\beta}) \right]. \tag{12}$$

Here the scalar order parameter $S = \langle \cos 3\psi \rangle$. This formula can be compared with the corresponding expression for the order parameter of the 2D nematic phase $S = \langle \cos 2\psi \rangle$. The orientational part of the tensor order parameter has exactly the same mathematical form as the molecular alignment tensor $t_{\alpha\beta\gamma}$ [see Eq. (6)] because both tensors represent the same symmetry group. One notes that the order parameter (12) is relatively cumbersome. However, the coupling between $T_{\alpha\beta\gamma}$ and the molecular alignment tensor can be expressed in a very simple form,

$$T_{\alpha\beta\gamma} t_{\alpha\beta\gamma} = \langle \cos 3\psi \rangle \cos 3\psi. \tag{13}$$

This means that the orientational distribution function, which may only depend on the coupling between a molecular orientation and the tensor order parameter, is indeed a function of $S \cos 3\psi$.

The tensor order parameter (12) can be used to show that the transition from the isotropic to the tripod phase can be of second order. Indeed, one can readily see that it is impossible to compose a cubic invariant in the Landau expansion of the free energy using a symmetric third-rank tensor.

Finally, one notes that so far we have considered only the order parameter of the homogeneously ordered tripod phase. The more complex phases, presented in Figs. 1(b) and 1(c) are composed of three different superlattices and a transition from the orientationally disordered phase involves both orientational and translational symmetry breaking. In this case, the order parameter of an ordered superlattice can be expressed as a set of three density waves,

$$\rho^{(j)}_{\alpha\beta\gamma} = \rho_0 e^{i\mathbf{k}_j \cdot \mathbf{r}} T_{\alpha\beta\gamma}, \tag{14}$$

where the tensor $T_{\alpha\beta\gamma}$ is given by Eq. (12) and the wave vectors $\mathbf{k}_j$ $(j=1,2,3)$ are shown in Fig. 2. The angle between any two vectors $\mathbf{k}_j$ is equal to $2\pi/3$ and the length $|\mathbf{k}_j| = 2\pi\sqrt{3}/a$, where a is the period of the underlying hexagonal lattice.

III. MOLECULAR MODEL AND MONTE CARLO SIMULATIONS

A. Intermolecular model interaction potential

Let us consider the intermolecular pair potential energy between two tripod molecules depicted in Fig. 2. As discussed in Sec. II, the orientation of a tripod molecule i can be specified by the two-dimensional unit vector $\hat{\mathbf{a}}_i$ which is in the direction of a molecular leg (see Fig. 2). In this paper, we consider flat tripod molecules which possess a threefold symmetry axis. In this case, all three legs of a given molecule are equivalent and the unit vector $\hat{\mathbf{a}}_i$ can be in the direction of any one of them. In the laboratory frame, the orientation of such a molecule can also be specified by the angle ψ_i between the vector $\hat{\mathbf{a}}_i$ and some macroscopic axis $\hat{\mathbf{x}}$. In general, the interaction potential between two tripod molecules i and j depends both on their unit orientation vectors $\hat{\mathbf{a}}_i$ and $\hat{\mathbf{a}}_j$ and on the intermolecular separation vector $\mathbf{r}_{ij}$. Thus the pair potential $U(i,j)$ is $U(\hat{\mathbf{a}}_i, \hat{\mathbf{a}}_j, \mathbf{r}_{ij})$. In a monolayer, all three vectors $\hat{\mathbf{a}}_i$, $\hat{\mathbf{a}}_j$, and $\mathbf{r}_{ij}$ are parallel to the same plane, and in this case the relative orientation of the two molecules can be specified by two angles ϕ_i and ϕ_j (see Fig. 2), which determine the orientation of the axes $\hat{\mathbf{a}}_i$ and $\hat{\mathbf{a}}_j$ with respect to the intermolecular separation vector $\mathbf{r}_{ij}$. Then the interaction potential is a function of the angles ϕ_i and ϕ_j and of the intermolecular distance r_{ij}, i.e., $U(i,j) = U(\phi_i, \phi_j, r_{ij})$. Here $\phi_i = \psi_i - \psi_{ij}$ and $\phi_j = \psi_j - \psi_{ij}$, where the angles ψ_i, ψ_j, and ψ_{ij} denote the orientation of the vectors $\hat{\mathbf{a}}_i$, $\hat{\mathbf{a}}_j$, and $\mathbf{r}_{ij}$, respectively, in the laboratory frame. For further considerations, it is more convenient to use the equivalent variables $\phi_i - \phi_j = \psi_i - \psi_j$ and $\phi_i + \phi_j = \psi_i + \psi_j - 2\psi_{ij}$. Here the angle $\phi_i - \phi_j$ specifies the relative orientation of the two flat molecules, which does not depend on the direction of the intermolecular separation vector (see Fig. 2).

The interaction potential should be a periodic function of the angles $\phi_i - \phi_j$ and $\phi_i + \phi_j$ and, therefore, it can be expanded in a double Fourier series. One notes that a flat molecule of C_3 symmetry coincides with itself after a rotation by an angle of $\pm 2\pi/3$ about the symmetry axis. The interaction potential between such molecules should be invariant under such rotations. Thus it follows from symmetry that the interaction potential must be invariant under the transformations $\phi_i' = \phi_i + 2\pi m/3$ and $\phi_j' = \phi_j + 2\pi n/3$, where m and n are integers. The corresponding transformation properties of the potential $U(\phi_i - \phi_j, \phi_i + \phi_j, r_{ij})$ can be expressed as $U(\phi_i - \phi_2 + 2\pi m/3, \phi_i + \phi_j + 2\pi n/3, r_{ij}) = U(\phi_i - \phi_j, \phi_i + \phi_j, r_{ij})$ for any m and n. One concludes that the Fourier expansion of the potential $U(\phi_i - \phi_j, \phi_i + \phi_j, r_{ij})$ contains only the functions $\cos[3m(\phi_i - \phi_j)]$ and $\cos[3n(\phi_i + \phi_j)]$. The functions $\sin[3m(\phi_i - \phi_j)]$ and $\sin[3n(\phi_i + \phi_j)]$ are not included because for nonchiral molecules the 2D interaction potential should be invariant under a simultaneous sign inversion of the angles ϕ_i and ϕ_j. Thus any interaction between two tripod molecules can be expanded as

$$U(\phi_i - \phi_j, \phi_i + \phi_j, r_{ij}) = \sum_{m,n=0}^{\infty} U_{mn}(r_{ij}) \cos[3m(\phi_i - \phi_j)] \cos[3n(\phi_i + \phi_j)]. \tag{15}$$

Taking into consideration only the first terms of this expansion, one obtains the following simple model interaction potential:

$$U(i,j) = U_0(r_{ij}) + U_-(r_{ij}) \cos[3(\phi_i - \phi_j)] + U_+(r_{ij}) \cos[3(\phi_i + \phi_j)]. \tag{16}$$

In this and in the following section, we show that the model potential (16) can be used both in computer simulations and in a mean-field theory to obtain the structures presented in Fig. 1.

Let us first consider the 2D phase with homogeneous orientational order (structure *A* in Fig. 1). In this phase all molecules, on an average, are parallel to each other, and a simple interaction potential that stabilizes this structure is provided by the second term in Eq. (16), with a negative coupling constant ($U_- < 0$). Thus the model potential for structure *A* can be written as

$$U_A(i,j) = U_0(r_{ij}) - U_A(r_{ij})\cos[3(\phi_i - \phi_j)]. \qquad (17)$$

For $U_A > 0$, the potential takes its minimum for $\phi_i = \phi_j$, i.e., for parallel molecules. We note that in this potential the threefold molecular symmetry is reflected in the function $\cos[3(\phi_i - \phi_j)]$, which has the periodicity of $2\pi/3$. The analogous potential for a 2D system of rodlike molecules (which possess a C_2 symmetry axis) would be of the form $U(i,j) = U_0(r_{ij}) - J \cos[2(\phi_i - \phi_j)]$. This potential is characterized by the period π and is a 2D analog of the so-called Maier-Saupe interaction potential for rodlike molecules, known in the theory of liquid crystals [1].

The physical meaning of the potential (17) is that all three legs of two neighboring tripod molecules want to be parallel to each other, independent of their orientation with respect to the intermolecular separation vector, e.g., due to a long-range anisotropic attractive interaction. This can be reasonable if the legs are sufficiently short and, as a result, any two nearest neighbors on the hexagonal lattice (see Fig. 1) can rotate freely with respect to each other. For longer legs, there exists a strong repulsion between neighbor tripod molecules, which corresponds to interpenetration of the two legs. This repulsion takes place at some particular relative orientation of the two molecules with respect to the intermolecular separation vector, and it can be accounted for by the third term in Eq. (16).

Let us consider in more detail the interaction between two molecules depicted in Fig. 2, assuming that the legs are sufficiently long to overlap at some particular orientations. On one hand, the neighboring tails with long axes $\mathbf{a}_{1i}$ and $\mathbf{a}_{2j}$ (see Fig. 2) want to be parallel due to the anisotropic attractive dispersion interaction. Thus the interaction potential is expected to take its minimum for $\phi_i - \phi_j = \pi/6$, i.e., for antiparallel orientation of the vectors $\mathbf{a}_{1i}$ and $\mathbf{a}_{2j}$ in Fig. 2. This can be achieved if the coupling constant U_- is positive.

On the other hand, there should be a strong repulsion between the two molecules if the two neighboring tails overlap, i.e., if both $\mathbf{a}_{1i}$ and $\mathbf{a}_{2j}$ in Fig. 2 are in the direction of the intermolecular separation vector $\mathbf{r}_{ij}$. In this configuration, $\phi_i = 0$ and $\phi_j = \pi$. The repulsion between two tripod molecules due to an overlap of the neighboring tails is described by the third term in Eq. (16). For $\phi_i = 0$ and $\phi_j = \pi$, one obtains $U_+ \cos[3(\phi_i + \phi_j)] = -U_+$ and therefore the coupling constant U_+ should be negative.

One concludes that in the first approximation, the interaction between two tripod molecules can qualitatively be described by the simple model potential (16). The ratio and the signs of the coupling constants U_- and U_+ are expected to depend on the length of the molecular side chain. For sufficiently long chains, which may overlap at some particular relative orientations of the two molecules, the constants $U_- > 0$ and $U_+ < 0$. It is shown in Sec. III B below that the experimentally observed structure *B* presented in Fig. 1 can be obtained in computer simulations using the model potential (16). A simple mean-field theory of such an anisotropic 2D phase, based on the same pair potential (16), is presented in Sec. IV.

We note that the properties of an anisotropic two-dimensional phase, composed of tripod molecules with sufficiently long tails, are determined by frustration. In fact, it is generally impossible to find a homogeneous orientation of all molecules which corresponds to a minimum of the interaction potential for all pairs of nearest neighbors. The interaction energy between two parallel tripod molecules strongly depends on the orientation of the molecular axes with respect to the intermolecular vector as can be seen from the structure of potential (16). For example, for $\phi_i = \phi_j = 0$ the interaction energy $U(i,j) = U_0 + U_- + U_+$, while for $\phi_i = \phi_j = \pi/2$ one obtains $U(i,j) = U_0 + U_- - U_+$. Thus, even if the interaction energy is negative for a given pair of nearest neighbors, it may be positive for some other pair due to a repulsion of interfering tails. For instance, we observe the honeycomblike structure *C* in Fig. 1 in computer simulations, when assuming both U_+ and U_- to be positive.

As a further simplification, we consider only interactions between nearest neighbors and assume that the molecular centers are located on the sites of a hexagonal lattice as it has been observed in experiment [11]. The hexagonal lattice apparently results from an interaction between flat molecules and a graphite substrate, and there is no experimental indication of the existence of a fluid phase. Thus we consider only two-dimensional plastic crystal phases in which the anisotropic molecules possess one orientational degree of freedom.

B. Monte Carlo simulations

In order to examine the stability of the structures in Fig. 1 we performed 2D Monte Carlo computer simulations for a model system consisting of 1200 tripod molecules. The molecular centers of mass were fixed on the sites of a hexagonal lattice, whereas the tripods were allowed to rotate freely in plane about their C_3 symmetry axes. The system was placed into a simulation box of the hexagonal shape (see Fig. 7) which reflects the symmetry of the underlying lattice model. Periodic boundary conditions in all three directions were employed by surrounding the simulation box with a chain of outer molecules. These were periodic images of molecules inside the box, shifted by one box period in the appropriate direction. The Monte Carlo simulations were performed for various temperatures between 0.1 and 3.0, with a temperature interval of 0.1. For each temperature, the simulation run consisted of 5000 equilibration cycles followed by another 5000 cycles to evaluate the average order parameters and overall orientations. For controlling thermodynamic equilib-

TABLE I. Dimensionless parametrizations of the model interaction potential between a pair of tripod molecules corresponding to the structures in Fig. 1.

Structure of Fig.1	Parameter U_-	Parameter U_+
A	-1	0
B	1	-1
C	1	1

rium, both the instantaneous energy and the order parameter and overall orientation were monitored each tenth of the Monte Carlo cycle.

The tripod molecules were interacting via the pair potential (16) introduced in the preceding section. Only nearest neighbor interactions were taken into account, i.e., the total interaction of one molecule was the sum of six pair interactions. Due to periodic boundary conditions, the molecules on the boundary of the box interacted both with real and image molecules. As already discussed, we chose three distinct parametrizations of the model potential (16) to investigate the different phases of Fig. 1. Because the molecules are fixed on lattice sites and the nearest neighbor distance is a constant, there is no dependence of the potential parameters on the intermolecular scalar distance r_{ij}. Therefore, the parameter U_0 merely denotes an arbitrary shift of the energy reference point. We set it equal to zero. The choice of the parameters U_- and U_+, corresponding to the structures *A*, *B*, and *C* of Fig. 1, is summarized in Table I.

For a detailed investigation, we calculated the temperature dependence of the scalar order parameter $S=\langle\cos 3\chi_i\rangle$ from the simulation data. Here χ_i denotes the angle between the $\hat{\mathbf{a}}_{1i}$ axis of an individual tripod molecule and the average preferred orientation $\hat{\mathbf{n}}$. Apparently, *S* cannot be evaluated from its definition, because the director axis $\hat{\mathbf{n}}$ is not known *a priori*. In the following, we derive a procedure of how to determine both the scalar order parameter and the director from simulations. As a starting point, we state that the orientations of the molecular axes $\hat{\mathbf{a}}_{1i}$ are known in the laboratory frame, where $\psi_{ix}=\psi_i$ and $\psi_{iy}=\pi/2-\psi_i$ are the angles between $\hat{\mathbf{a}}_{1i}$ and the *x* and the *y* axis, respectively. Due to trigonometric identities, we can evaluate the averages

$$\langle\cos 3\psi_{ix}\rangle=4\langle(\hat{\mathbf{a}}_{1i}\cdot\hat{\mathbf{x}})^3\rangle-3\langle(\hat{\mathbf{a}}_{1i}\cdot\hat{\mathbf{x}})\rangle, \tag{18}$$

$$\langle\cos 3\psi_{iy}\rangle=4\langle(\hat{\mathbf{a}}_{1i}\cdot\hat{\mathbf{y}})^3\rangle-3\langle(\hat{\mathbf{a}}_{1i}\cdot\hat{\mathbf{y}})\rangle. \tag{19}$$

Now we express the unit vectors $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ of the laboratory frame in the orthonormal frame $(\hat{\mathbf{n}},\hat{\mathbf{n}}_\perp)$ spanned by the director and the vector $\hat{\mathbf{n}}_\perp$ perpendicular to the director,

$$\hat{\mathbf{x}}=\hat{\mathbf{n}}\cos\Psi_n+\hat{\mathbf{n}}_\perp\sin\Psi_n, \tag{20}$$

$$\hat{\mathbf{y}}=\hat{\mathbf{n}}\sin\Psi_n-\hat{\mathbf{n}}_\perp\cos\Psi_n. \tag{21}$$

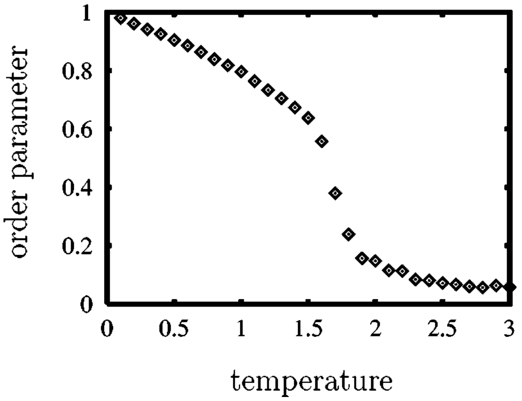

FIG. 3. Scalar order parameter *S* vs dimensionless temperature *T* for potential parametrizations $U_-=-1$ and $U_+=0$ (in dimensionless units), corresponding to structure *A* of Fig. 1.

Here $\Psi_n=\chi_i-\psi_i$ denotes the angle between the director and the *x* axis. After inserting Eqs. (20), (21) into Eqs. (18), (19) and some trigonometric algebra, we find

$$\langle\cos 3\psi_{ix}\rangle=\cos 3\Psi_n\langle\cos 3\psi_i\rangle=S\ \cos 3\Psi_n, \tag{22}$$

$$\langle\cos 3\psi_{iy}\rangle=\sin 3\Psi_n\langle\cos 3\psi_i\rangle=S\ \sin 3\Psi_n. \tag{23}$$

The equations above now enable us to determine the scalar order parameter *S* and the angle Ψ_n which describes the director orientation, from averages calculated in the laboratory system,

$$S=\sqrt{\langle\cos 3\psi_{ix}\rangle^2+\langle\cos 3\psi_{iy}\rangle^2}, \tag{24}$$

$$\Psi_n=\frac{1}{3}\arctan\frac{\langle\cos 3\psi_{iy}\rangle}{\langle\cos 3\psi_{ix}\rangle}=\frac{1}{3}\ \mathrm{arccot}\frac{\langle\cos 3\psi_{ix}\rangle}{\langle\cos 3\psi_{iy}\rangle}. \tag{25}$$

We start the discussion of the simulation results with the parametrizations $U_-=-1$ and $U_+=0$ which yield the homogeneous structure *A* (see Fig. 1). Here all molecular axes are, on an average, parallel to each other. Figure 3 shows the temperature dependence of the scalar order parameter. It is

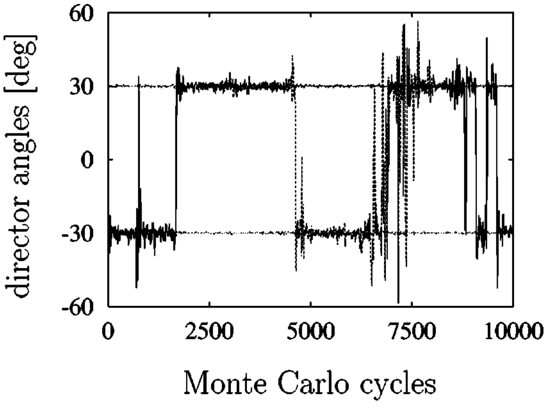

FIG. 4. Instantaneous director angles during a Monte Carlo run at temperature $T=0.1$ for potential parametrization $U_-=1$ and $U_+=-1$ (in dimensionless units). Solid, dashed, and dotted lines correspond to the three superlattices in Fig. 3.

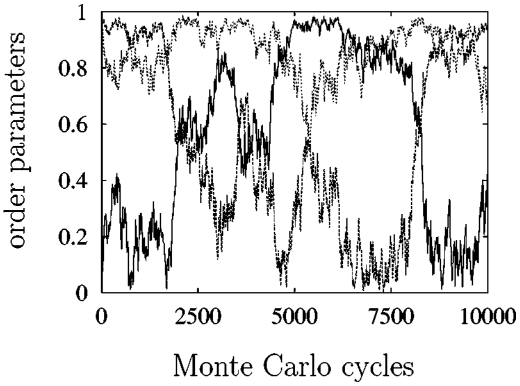

FIG. 5. Instantaneous order parameters during a Monte Carlo run at temperature $T=0.1$ for potential parametrizations $U_-=1$ and $U_+=-1$ (in dimensionless units). Solid, dashed, and dotted lines correspond to the three superlattices of Fig. 3.

close to 1 for very low temperatures and then decays with increasing temperature. The transition to the isotropic phase is at about $T_c=1.9$. This value is considerably smaller than the mean-field transition temperature of $T_c=3.0$. We will discuss this discrepancy further in the following Section. Due to limited system size the order parameter in the isotropic phase retains small, but finite values.

Structures *B* and *C* of Fig. 1 are more complicated. As explained in the preceding section, they can be described as a superposition of the three superlattices imposed on the basic hexagonal lattice. The superlattices are distinguished by different average orientational order of the respective molecules. To investigate this behavior, we calculated the order parameter *S* and the director angle Ψ_n from Eqs. (24) and (25) separately on the three superlattices. A very interesting feature of the system is revealed from Figs. 4 and 5 which plot the average director angles and the scalar order parameters for the three superlattices during the Monte Carlo run (parametrizations $U_-=1$, $U_+=-1$, temperature $T=0.1$). Obviously, there are two superlattices with clearly defined director angles of $\pm 30°$, while the average orientation on the third superlattice is strongly fluctuating (Fig. 4). However, the superlattices themselves are not permanent. Instead, they are interchanging their rôles. E.g., the superlattice whose orientation fluctuates around $-30°$ at the beginning of the simulation run assumes a stable orientation of $+30°$ by a jump after 1500 cycles. To analyze the orientational order on the superlattices, we thus decided to sort the order parameters in Fig. 5 according to their magnitude for each Monte Carlo cycle. The averages over the run were then calculated from the sorted order parameters. In this way, we obtained a maximum, medium, and minimum order parameter.

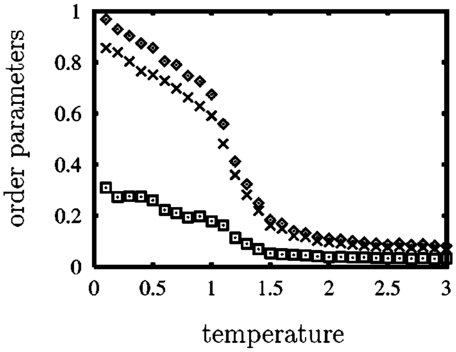

FIG. 6. Scalar order parameters *S* vs dimensionless temperature *T* for potential parametrizations $U_-=1$ and $U_+=-1$ (in dimensionless units), corresponding to structure *B* of Fig. 1. Rhombs, × symbols and squares correspond to three different sublattices.

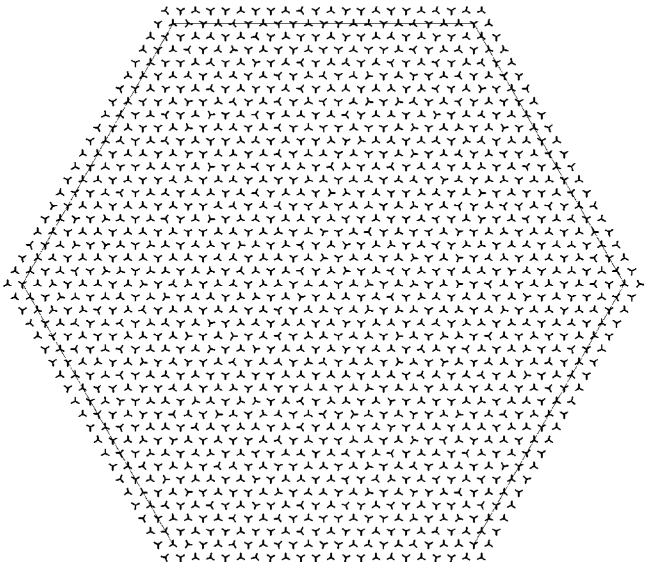

FIG. 7. Molecular configuration from a Monte Carlo run at temperature $T=0.1$ for potential parametrizations $U_-=1$ and $U_+=-1$, corresponding to structure *B* in Fig. 1. The hexagonal simulation box contains 1200 tripod molecules. A chain of periodic image molecules outside the box is also shown.

In Fig. 6, the temperature dependence of the three order parameters introduced above is plotted for potential parameters $U_-=1$, $U_+=-1$. In the low temperature regime, the plot clearly reveals that the maximum and medium order parameters are quite high compared to the minimum one. The latter corresponds to the disordered superlattice, i.e., the strong fluctuations of the director angle in Fig. 4. On the

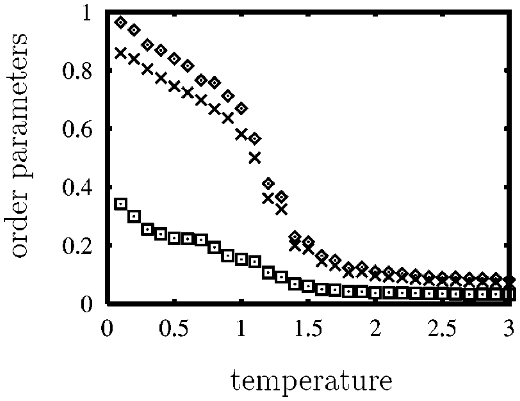

FIG. 8. Scalar order parameters *S* vs dimensionless temperature *T* for potential parametrizations $U_-=1$ and $U_+=1$, corresponding to structure *C* of Fig. 1. Rhombs, × symbols and squares correspond to three different sublattices.

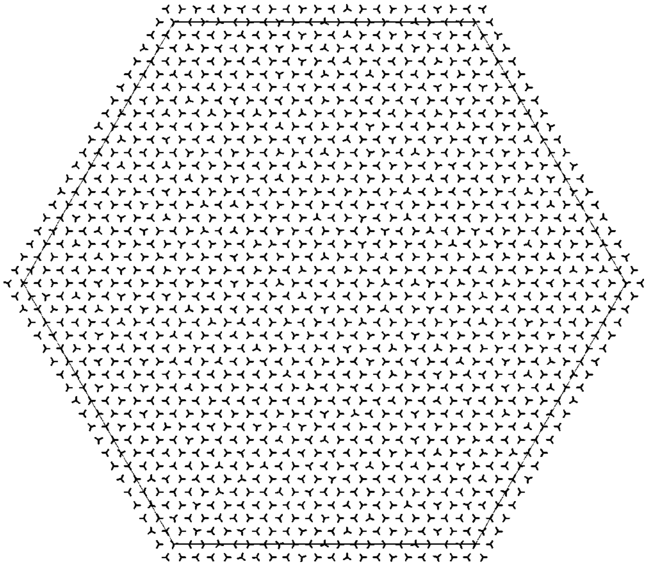

FIG. 9. Molecular configuration from a Monte Carlo run at temperature $T=0.1$ for potential parametrisation $U_-=1$ and $U_+=1$, corresponding to structure C of Fig. 1. The hexagonal simulation box contains 1200 tripod molecules. A chain of periodic image molecules outside the box is also shown.

other hand, the molecules on the remaining two superlattices are well aligned at director angles of $\pm 30°$, respectively. They cause the maximum and medium order parameters to assume high values which are close to each other (Fig. 6). All together, this exactly corresponds to the structure observed by Charra and Cousty in the 2D system of discotic molecules [11]. This structure is presented in Fig. 1 (structure B). Thus our model potential is sufficient to stabilize this unusual partly disordered structure in Monte Carlo simulations. With increasing temperature the order is again decreasing, similar to the homogeneous structure A (Fig. 3). The phase transition now occurs at a lower temperature. Above $T_c=1.5$, the order in all superlattices is mainly lost. A snapshot of the molecular configuration for the system at temperature $T=0.1$ is presented in Fig. 7.

Finally, we consider the potential parametrization $U_-=U_+=1$. The simulation results are analyzed in the same way as in the previous case, namely, by sorting the order parameters on the three superlattices according to their magnitude. The temperature dependence of these sorted order parameters is fairly similar to the one corresponding to structure B (Fig. 8). Again, in the low temperature regime there are two superlattices with high order parameters while the order in the third one is low. The director angles in the ordered superlattices now are $\pm 60°$, which means that these molecules are aligned according to the crystallographic axes of the hexagonal lattice. As a result, the phase appears to be nonchiral. The disordered superlattice corresponds to a frustration effect: the molecules in the centers of the hexagons which are formed by the remaining two superlattices are orientationally disordered because this is the only way to reduce the total free energy of the whole system (structure C in Fig. 1). Again, a snapshot of the configuration at temperature $T=0.1$ is shown in Fig. 9. The frustration of the molecules on the disordered superlattice is clearly recognizable. We notice that even at low temperatures the structure is not perfect, instead, some defects are forming.

IV. MOLECULAR-STATISTICAL THEORY

Let us first consider the simple structure A presented in Fig. 1. This structure corresponds to the anisotropic 2D phase in which all lattice sites are statistically equivalent. From the molecular-statistical point of view, the phase A is characterized by the one-particle distribution function $f_1(\psi_j)$, where the angle ψ_j specifies the orientation of the tripod molecule i in the laboratory frame. By contrast, the phase B in Fig. 1 is composed of three inequivalent superlattices which are characterized by different average orientations of the tripod molecules. Such a phase is described by three different orientational distribution functions $f_1^{(s)}(\psi_j)$ $(s=1,2,3)$, which correspond to the three inequivalent superlattices. It should be noted that all sites in all three superlattices in the phase B are still occupied by equivalent molecules and thus the pair interaction potential $U(i,j)$ remains the same for all pairs of nearest neighbors. The general form of this potential is given by Eq. (15). In this section, we will use the simple model potential (16) which is obtained by taking into account the first terms in expansion (15). The same model potential has been used in the simulations (see Sec. III).

Taking into account only interactions between nearest neighbors, the internal energy U per molecule can be expressed as a sum of averaged interaction energies between all pairs of neighboring molecules. One notes that in the phase B any two nearest neighbors belong to different superlattices. Thus there exist only three inequivalent pairs of nearest neighbors which we denote as (1,2), (2,3), and (1,3), where the indices i and j $(i,j=1,2,3)$ correspond to different superlattices. Each molecule which belongs to an arbitrary superlattice i is interacting with three nearest neighbors belonging to the superlattice $j\neq i$, and with three nearest neighbors belonging to the superlattice $k\neq j\neq i$. Now the internal energy U of the phase B in the mean-field approximation can be written as

$$\begin{aligned}U/N=&3\int f_1^{(1)}(\psi_1)U(\psi_1-\psi_2,\psi_1+\psi_2-2\psi_{12})\\&\times f_1^{(2)}(\psi_2)d\psi_1 d\psi_2\\&+3\int f_1^{(1)}(\psi_1)U(\psi_1-\psi_3,\psi_1+\psi_3-2\psi_{13})\\&\times f_1^{(3)}(\psi_3)d\psi_1 d\psi_3\\&+3\int f_1^{(2)}(\psi_2)U(\psi_2-\psi_3,\psi_2+\psi_3-2\psi_{23})\\&\times f_1^{(3)}(\psi_3)d\psi_2 d\psi_3,\end{aligned} \tag{26}$$

where the angle ψ_i specifies the orientation of molecule i and the angle ψ_{ij} specifies the orientation of the intermolecular vector between the neighboring molecules i and j. Here

$f_1^{(i)}(\psi_i)$ is the orientational distribution function of the superlattice *i*, and the pair interaction potential $U(i,j)=U(\psi_i-\psi_j,\psi_i+\psi_j-2\psi_{ij})$ is given by Eq. (16).

Now the free energy F can be determined using the general thermodynamic expression

$$U=\frac{\partial(\beta F)}{\partial\beta}, \tag{27}$$

where $\beta=1/(k_BT)$ and where the internal energy U is given by Eq. (26). The solution of Eq. (27) can be expressed as

$$\begin{aligned}F/N={}&k_BT\int f_1^{(1)}(\psi_1)\ln\, f_1^{(1)}(\psi_1)d\psi_1\\&+k_BT\int f_1^{(2)}(\psi_2)\ln\, f_1^{(2)}(\psi_2)d\psi_2\\&+k_BT\int f_1^{(3)}(\psi_3)\ln\, f_1^{(3)}(\psi_3)d\psi_2+3U_{12}+3U_{13}\\&+3U_{23},\end{aligned} \tag{28}$$

where

$$U_{ij}=\int f_1^{(i)}(\psi_i)U(\psi_i-\psi_j,\psi_i+\psi_j-2\psi_{ij})f_1^{(j)}(\psi_j)d\psi_i d\psi_j, \tag{29}$$

and where $i\neq j$ $(i,j=1,2,3)$. One notes that Eq. (26) for the internal energy U can now be derived back from Eqs. (27)–(29), taking into account that the distribution functions $f_1^{(i)}(\psi_i)$ should correspond to the minimum of the free energy functional (28). Minimization of the free energy yields the following equations for the orientational distribution functions:

$$f_1^{(i)}(\psi_i)=\frac{1}{Z_i}\exp\{-\beta U_{MF}^{(i)}(\psi_i)\}, \tag{30}$$

where the mean-field potentials $U_{MF}^{(i)}(\psi_i)$ are given by

$$\begin{aligned}U_{MF}^{(1)}(\psi_1)={}&3\int U(\psi_1-\psi_2,\psi_1+\psi_2-2\psi_{12})f_1^{(2)}(\psi_2)d\psi_2\\&+3\int U(\psi_1-\psi_3,\psi_1+\psi_3-2\psi_{13})f_1^{(3)}(\psi_3)d\psi_3,\end{aligned} \tag{31}$$

$$\begin{aligned}U_{MF}^{(2)}(\psi_2)={}&3\int U(\psi_2-\psi_1,\psi_2+\psi_1-2\psi_{12})f_1^{(1)}(\psi_1)d\psi_1\\&+3\int U(\psi_2-\psi_3,\psi_2+\psi_3-2\psi_{23})f_1^{(3)}(\psi_3)d\psi_3,\end{aligned} \tag{32}$$

$$\begin{aligned}U_{MF}^{(3)}(\psi_3)={}&3\int U(\psi_3-\psi_1,\psi_3+\psi_1-2\psi_{13})f_1^{(1)}(\psi_1)d\psi_1\\&+3\int U(\psi_3-\psi_2,\psi_3+\psi_2-2\psi_{23})f_1^{(2)}(\psi_2)d\psi_2,\end{aligned} \tag{33}$$

with the pair interaction potential

$$\begin{aligned}U(i,j)={}&U_0(r_{ij})+U_-(r_{ij})\cos[3(\psi_i-\psi_j)]\\&+U_+(r_{ij})\cos[3(\psi_i+\psi_j-2\psi_{ij})].\end{aligned} \tag{34}$$

As discussed in Sec. II, the orientational distribution functions $f_1^{(i)}=f_1^{(i)}(\cos 3\psi_i)$ because they should depend only on the coupling between the molecular axes $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ and the third-rank tensor order parameter $T_{\alpha\beta\gamma}$ [see Eq. (13)] of the phase *B*. Here ψ_i is the angle between a molecular axis $\mathbf{a}_i$ and a macroscopic director $\mathbf{l}_i$. It is important to note that, due to the symmetry of the phase, one may use any director from the set ($\mathbf{l}_1$, $\mathbf{l}_2$, $\mathbf{l}_3$) without changing the mathematical form of the free energy functional (28).

The expression for the pair interaction potential (34) $U(\psi_i-\psi_j,\psi_i+\psi_j-2\psi_{ij})$ can be simplified if one considers only the interactions between the nearest neighbors on the hexagonal lattice. In this case, $6\psi_{ij}=2\pi n$ for all pairs of nearest neighbors (i,j), where n is an integer. As a result, the second term in Eq. (34) can be rewritten as $U_+\cos[3(\psi_i+\psi_j-2\psi_{ij})]=U_+\cos(3\psi_i+3\psi_j+2\pi n)=U_+\cos[3(\psi_i+\psi_j)]$, i.e., the pair potential does not depend on the "bond" angle ψ_{ij} in this case and can finally be expressed as

$$\begin{aligned}U(i,j)={}&U_0(r_{ij})+U_+\cos[3(\psi_i+\psi_j)]\\&+U_-\cos[3(\psi_i-\psi_j)].\end{aligned} \tag{35}$$

Now one should take into account that different superlattices may be characterized by different average orientations of the tripod molecules. In other words, different superlattices may correspond to distinct directors. In this case, the orientational distribution functions $f_1^{(i)}(\psi)$ actually depend on the difference $\psi-\psi_{i0}$, where the angle ψ_{i0} specifies the orientation of the director of the superlattice *i* in the laboratory frame. Thus $f_1^{(i)}(\psi)=f_1^{(i)}(\psi-\psi_{i0})=f_1^{(i)}(\cos 3(\psi-\psi_{i0}))$. Substituting this expression together with Eq. (35) into Eq. (31), one obtains

$$\begin{aligned}U_{MF}^{(i)}(\psi_i)={}&3U_+\cos[3(\psi_i+\psi_{j0})]S_j+3U_-\\&\times\cos[3(\psi_i-\psi_{j0})]S_j+3U_+\\&\times\cos[3(\psi_i+\psi_{k0})]S_k+3U_-\\&\times\cos[3(\psi_i-\psi_{k0})]S_k,\end{aligned} \tag{36}$$

where $i\neq j\neq k$ $(i,j,k=1,2,3)$ and S_i are the corresponding orientational order parameters given by the following equation:

$$S_i=\int \cos 3[(\psi-\psi_{i0})]f_1^{(i)}(\psi-\psi_{i0})d\psi_{i0}. \tag{37}$$

In the derivation of Eqs. (36) and (37), we have taken into consideration that the identity

$$\int \cos 3(\psi_i \pm \psi_j) f_1(\psi_j - \psi_{j0}) d\psi_j = \cos[3(\psi_i \mp \psi_{j0})] \int \cos[3(\psi_j - \psi_{j0})] f_1(\psi_j - \psi_{j0}) d\psi_j \tag{38}$$

is valid for any function f which is even in $\psi_j - \psi_{j0}$.

One notes that the angles ψ_{j0} in Eq. (36) are not arbitrary. It is possible to obtain equations for the angles from the general equations (30) and (36). Indeed, let us substitute the mean-field potentials (36) into Eq. (30). It follows that the orientational distribution function $f_1^{(i)}$ on the left-hand side of Eq. (30) depends on $\psi_i - \psi_{i0}$ $(i=1,2,3)$ or, more exactly, on $\cos[3(\psi_i - \psi_{i0})]$, as discussed before. At the same time, the corresponding mean-field potential on the right-hand side of Eq. (30) depends on $\cos[3(\psi_i \pm \psi_{j0})]$, where $j \neq i$. However, the dependence should be the same on both sides of Eq. (30), and this imposes some restrictions on the values of the angles ψ_{0i} $(i=1,2,3)$. As a result, one obtains the following equations for ψ_{0i},

$$\sin[3(\psi_{i0} + \psi_{j0})] = 0, \tag{39}$$

$$\sin[3(\psi_{i0} - \psi_{j0})] = 0. \tag{40}$$

Now Eq. (36) can be rewritten in the form

$$U_{MF}^{(i)}(\psi) = (U_{ij} S_j + U_{ik} S_k) \cos[3(\psi - \psi_{i0})], \tag{41}$$

where

$$U_{ij} = 3U_+ \cos[3(\psi_{i0} + \psi_{j0})] + 3U_- \cos[3(\psi_{i0} - \psi_{j0})], \tag{42}$$

$$U_{ik} = 3U_+ \cos[3(\psi_{i0} + \psi_{k0})] + 3U_- \cos[3(\psi_{i0} - \psi_{k0})]. \tag{43}$$

One notes that Eq. (39) should be valid for all $i \neq j$ $(i,j = 1,2,3)$. It can be shown that there exist three different solutions of Eq. (39) which correspond to different phases.

(1) $\psi_{01} = \psi_{02} = \psi_{03} = \pi/2 + (2\pi/3)n$. All three sublattices are ordered in the same direction. Substituting this solution into Eqs. (41)–(43), one obtains the following expression for the mean-field potentials:

$$U_{MF}^{(i)}(\psi_i) = 3(U_- - U_+) \cos[3(\psi_i - \pi/2)](S_j + S_k), \tag{44}$$

where $i \neq j \neq k$. Here the orientational order parameters S_i can be determined self-consistently after substitution of Eqs. (42) and (43) into Eq. (37). One notes that in this case, all three superlattices are equivalent and thus the only solution is $S_1 = S_2 = S_3 = S$, where

$$S = \frac{1}{Z_0} \int \cos 3\psi \exp\{-6\beta(U_- - U_+) \cos 3\psi\} d\psi \tag{45}$$

and

$$Z_0 = \int \exp\{-6\beta(U_- - U_+) \cos 3\psi\} d\psi. \tag{46}$$

Equations (42) and (43) describe a second-order orientational phase transition and their numerical solution is presented in Fig. 1. Thus in this case, the system undergoes a phase transition into the homogeneously orientationally ordered phase which does not split into sublattices. This phase corresponds to structure A in Fig. 2. One notes that the homogeneously ordered phase may be stable only if $U_- - U_+ < 0$, i.e., if the anisotropic attraction (characterized by the coupling constant U_-) is stronger than the anisotropic repulsion between the tripod molecules. The second-order phase transition from the 2D isotropic to the homogeneously ordered phase occurs at $k_B T_C = 3(U_+ - U_-)$.

(2) $\psi_{i0} = \pi/6 + 2\pi n/3$, $\psi_{j0} = -\pi/6 + 2\pi k/3$ $(i \neq j)$, where n and k are integers. In this case, the superlattices i and j are ordered in opposite directions. One notes that this is possible because the orientational order parameter of the tripod molecules is polar, as discussed in Sec. II. It should be noted that at this stage, the orientation of the principal axes of the third superlattice $k \neq j \neq i$ remains undetermined. It is shown below that the third superlattice is disordered.

Now let us substitute $\psi_{i0} = \pi/6 + 2\pi n/3$ and $\psi_{j0} = -\pi/6 + 2\pi k/3$ into the expression for the mean-field potential $U_{MF}^{(k)}$ of the superlattice k. One obtains

$$U_{MF}^{(k)}(\psi) = 3(U_+ - U_-)(S_j - S_i) \sin[3(\psi - \psi_{k0})]. \tag{47}$$

The order parameter S_k of the superlattice k is given by

$$S_k = \frac{1}{Z_k} \int \cos[3(\psi - \psi_{k0})] \exp\{-\beta U_{MF}^{(k)}(\psi)\} d\psi. \tag{48}$$

Now one can readily see that the mean-field potential $U_{MF}^{(k)}(\psi)$ vanishes if $S_i = S_j$ $(i \neq j \neq k)$, i.e., if the two other superlattices are characterized by the same scalar order parameter. In this case, the orientational distribution function $f_1^{(k)}(\psi)$ is isotropic and the corresponding order parameter $S_k = 0$. The solutions $S_i = S_j = S$ and $S_k = 0$ can be tested for self-consistency by using the equations for S_i and S_j,

$$S_i = \frac{1}{Z_i} \int \cos[3(\psi - \psi_{i0})] \exp\{-\beta U_{MF}^{(i)}(\psi)\} d\psi, \tag{49}$$

$$S_j = \frac{1}{Z_j} \int \cos[3(\psi - \psi_{j0})] \exp\{-\beta U_{MF}^{(j)}(\psi)\} d\psi, \tag{50}$$

where the mean-field potentials $U_{MF}^{(i)}$ and $U_{MF}^{(j)}$ are given by Eq. (41). Substituting $\psi_{0i} = \pi/6$, $\psi_{0j} = -\pi/6$, and $S_k = 0$ into Eqs. (42) and (43), one obtains

$$S_i = \frac{1}{Z_i} \int \cos 3\psi \exp\{-\beta(U_+ - U_-) S_j \cos 3\psi\} d\psi, \tag{51}$$

$$S_j = \frac{1}{Z_j}\int \cos 3\psi \exp\{-\beta(U_+ - U_-)S_i \cos 3\psi\} d\psi. \tag{52}$$

It is interesting to note that Eqs. (51) and (52) are completely equivalent, i.e., they are transformed into each other under an exchange of the indices *i* and *j*. Thus $S_i = S_j = S$, $S_k = 0$ is indeed a self-consistent solution of Eqs. (48)–(50), where the order parameter *S* is given by the single equation

$$S = \frac{1}{Z}\int \cos 3\psi \exp\{-\beta(U_+ - U_-)S \cos 3\psi\} d\psi \tag{53}$$

and where

$$Z = \int \exp\{-\beta(U_+ - U_-)S \cos 3\psi\} d\psi. \tag{54}$$

According to Eq. (53), the phase transition into the anisotropic tripod phase with three superlattices occurs at $T = T_0 = 2(U_- - U_+)/kB$. The transition is of second order. The phase is stable if $k_B T < 2(U_- - U_+)$, i.e., the coupling constant U_- should be larger than the constant U_+. One notes that the homogeneously ordered phase *A*, described above, is stable if $k_B T < 2(U_- - U_+)$ and therefore the phases *A* and *B* are complementary. For any fixed values of U_+ and U_-, these phases cannot occur simultaneously on the phase diagram.

(3) This solution corresponds to the phase *C* in Fig. 1 which has a "honeycomb" structure. In this case, the tripod molecules on the superlattices *i* and *j* are aligned in opposite directions, similar to the 2D chiral phase *B* discussed above. However, in the honeycomb phase, the directors of the two ordered superlattices are parallel to the axes of the underlying hexagonal lattice, while in the 2D chiral phase *B* they form an angle of $\pi/6$ with respect to the axes of the lattice. Now, using the same mathematical argument as in the description of the previous solution, it can be shown that $\psi_{i0} = \pi + 2\pi k/3$, $\psi_{j0} = 2\pi k/3$ into Eqs. (36), (37), and (30) yields the following solutions for the scalar order parameters of the three superlattices: $S_i = S_j = S$ and $S_k = 0$, where

$$S = \frac{1}{Z}\int \cos 3\psi \exp\{-\beta(U_+ + U_-)S \cos 3\psi\} d\psi \tag{55}$$

and

$$Z = \int \exp\{-\beta(U_+ + U_-)S \cos 3\psi\} d\psi. \tag{56}$$

Thus in the honeycomb phase, the third superlattice also appears to be disordered while the other two superlattices are characterized by the same scalar order parameter *S*. The directors of the two ordered superlattices point into opposite directions, similar to the phase *B*. In general, the honeycomb phase *C* is very similar to the phase *B*, but possesses a higher symmetry because all directors are parallel to the axes of the hexagonal lattice. As a result, the honeycomb phase appears to be nonchiral because it is invariant under a reflection with respect to any line which contains a lattice site and is parallel to one of the axes of the lattice.

One notes that Eq. (55) for the order parameter *S* has exactly the same mathematical form as Eqs. (53) and (45) for the phases *B* and *A*, respectively. The effective coupling constants, however, are different for all those phases, and thus these phases may be stable in different regions of the general $T - U_+ - U_-$ phase diagram. The honeycomb phase is stable for $k_B T < (U_+ - U_-)$.

V. CHIRAL ORDER PARAMETER OF THE INHOMOGENEOUS ANISOTROPIC PHASE

As discussed above, the inhomogeneous orientationally ordered phase *B* presented in Fig. 1(b) is two-dimensionally chiral. This means that it is not invariant under a reflection with respect to a line parallel to the plane of the structure. One notes, however, that no 2D structure can be chiral in the common three-dimensional sense because any 2D structure is invariant under a reflection with respect to the plane of the structure itself. In the 3D case, the chirality of a structure can be characterized by the so-called "chirality index" or the chiral order parameter which can be written in the general mathematical form [22,23]

$$\Delta_{3D} = \epsilon_{\alpha,\beta,\gamma} A_{\alpha,\beta,\gamma}, \tag{57}$$

where the nonsymmetric tensor $A_{\alpha,\beta,\gamma}$ characterizes the 3D structure and $\epsilon_{\alpha,\beta,\gamma}$ is the Levi-Cività tensor which is antisymmetric with respect to any two indices. The components of this tensor do not vanish if and only if $\alpha \neq \beta \neq \gamma$.

In the two-dimensional case, the chirality order parameter can generally be written as a coupling between the corresponding second-rank tensors:

$$\Delta_{2D} = \epsilon_{\alpha,\beta,} A_{\alpha,\beta}, \tag{58}$$

where $\epsilon_{\alpha,\beta}$ is the 2D unit antisymmetric tensor:

$$\epsilon_{\alpha,\beta} = -\epsilon_{\beta,\alpha}, \quad \epsilon_{xy} = 1, \tag{59}$$

where $\alpha,\beta = x,y$. One notes that the 2D tensor $\epsilon_{\alpha,\beta}$ is related to the Levi-Cività tensor: $\epsilon_{\alpha,\beta} = \epsilon_{\alpha,\beta,\gamma} e_\gamma$, where the unit vector $\mathbf{e}$ is normal to the plane. Thus the sign of the 2D antisymmetric tensor and the sign of the 2D chiral index depend on the choice of the direction of the normal to the plane. However, if the 2D chiral structure is located at an interface between two different media, the symmetry between $+\mathbf{e}$ and $-\mathbf{e}$ is broken and the whole system becomes 3D chiral. More information about 2D chirality indices can be found in Ref. [12].

Anisotropic organic monolayers composed of nonchiral molecules may become 2D chiral after a corresponding symmetry breaking phase transition [13–18]. The macroscopic chirality of such systems is usually determined by different orientations of several ordering tensors or by the spontaneous chiral orientational deformations. Recently, expressions for chiral order parameters for such systems have been proposed by Selinger *et al.* [24,25]. Using a similar approach, we propose the following expression for the chiral order parameter of the phase *B*:

$$\Delta_B=\frac{1}{l^3 N_0}\left\langle \sum_{i,j} \epsilon_{\alpha\beta}R^{(i,j)}_{\alpha\delta\gamma}(t^{(i)}_{\beta\delta\gamma}-t^{(j)}_{\beta\delta\gamma})\right\rangle, \tag{60}$$

where the brackets $\langle\cdots\rangle$ denote the ensemble average over the whole system, l is the length of the elementary bond on the hexagonal lattice, and N_0 is the total number of pairs of molecules in the system. Here the tensors $t^{(i)}_{\beta\delta\gamma}$ and $t^{(j)}_{\beta\delta\gamma}$, which are given by Eq. (6), specify the orientation of the tripod molecules i and j, respectively. The tensor $R^{(i,j)}_{\alpha\delta\gamma}$ is composed of the components of the intermolecular vector $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ and has the same mathematical structure given by Eq. (6). The chiral order parameter Δ_B is a 2D pseudoscalar which changes sign under a reflection with respect to a line in the plane of the structure. Equation (60) is also symmetric with respect to an interchange of the indices i and j because the tensor $R^{(i,j)}_{\alpha\delta\gamma}$ is odd in $\mathbf{r}_{ij}$. One notes that in a homogeneous system, the order parameter (60) vanishes identically. However, in the phase B the chiral order parameter is nonzero because the translational symmetry has been broken, and molecules i and j may belong to different sublattices with different tensor order parameters. In this paper, we consider a model in which the centers of tripod molecules are located on the sites on the hexagonal lattice. In this case, all intermolecular vectors $\mathbf{r}_{ij}$ are fixed in space. Taking into consideration only elementary bonds, i.e., the intermolecular vectors between the nearest neighbors, and using the properties of tensors (6), Eq. (60) can be rewritten in the simple scalar form [26]

$$\Delta_B=\frac{1}{N_0}\left\langle \frac{1}{2}\sum_{i,j}\{\sin[3(\psi_i-\psi_{ij})]-\sin[3(\psi_j-\psi_{ij})]\}\right\rangle, \tag{61}$$

where the angles ψ_i,ψ_j specify the orientation of the tripod molecules i and j, respectively, angle ψ_{ij} specifies the orientation of the bond (see Sec. III). On the other hand, the ensemble averaging in Eq. (61) can be performed directly in the tensor form:

$$\begin{aligned}\Delta_B&=\tfrac{1}{6}\epsilon_{\alpha\beta}R^{o}_{\alpha\delta\gamma}(\langle t^{\mathrm{I}}_{\beta\delta\gamma}\rangle-\langle t^{\mathrm{II}}_{\beta\delta\gamma}\rangle+\langle t^{\mathrm{III}}_{\beta\delta\gamma}\rangle)\\&=\tfrac{1}{6}\epsilon_{\alpha\beta}R^{o}_{\alpha\delta\gamma}(T^{\mathrm{I}}_{\beta\delta\gamma}-T^{\mathrm{II}}_{\beta\delta\gamma}),\end{aligned} \tag{62}$$

where $T^{\mathrm{I}}_{\beta\delta\gamma}$ and $T^{\mathrm{II}}_{\beta\delta\gamma}$ are the tensor order parameters of the sublattices "1" and "2," respectively, which are given by the general equation (12) but may depend on different directors $\mathbf{n}_{\mathrm{I}}$ and $\mathbf{n}_{\mathrm{II}}$. The sublattice "3" is orientationally disordered in the phase B and therefore $T^{\mathrm{III}}_{\beta\delta\gamma}=0$. The tensor $R^{o}_{\alpha\delta\gamma}$ has the same mathematical form as in Eq. (6) but it depends on the components of the unit vector $\mathbf{k}$ in the direction of a crystallographic axis of the hexagonal lattice (see Fig. 10):

$$R^{o}_{\alpha\beta\gamma}=k_\alpha k_\beta k_\gamma-\tfrac{1}{4}(k_\alpha\delta_{\beta\gamma}+k_\beta\delta_{\alpha\gamma}+k_\gamma\delta_{\alpha\beta}). \tag{63}$$

Taking into account that $R^{o}_{\alpha\delta\gamma}T_{\alpha\delta\gamma}=\sin 3\phi_{kn}$, where ϕ_{kn} is the angle between the vectors $\mathbf{k}$ and $\mathbf{n}$, the chiral order parameter of the phase B can be written in the following simple form:

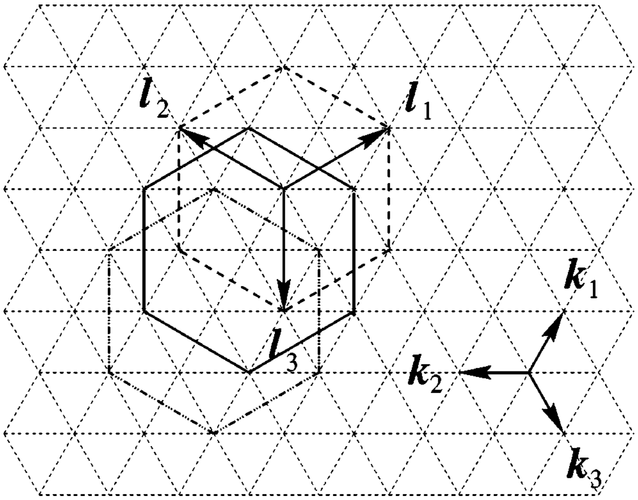

FIG. 10. Three superlattices characteristic for the structures B and C in Fig. 1. The vectors $\mathbf{k}_i$ specify the crystallographic directions of the basic hexagonal lattice. The superlattices are defined by the vectors $\mathbf{l}_i$.

$$\Delta_B=\tfrac{1}{6}[\sin(3\psi_{\mathrm{I0}})S_{\mathrm{I}}-\sin(3\psi_{0\mathrm{II}})S_{\mathrm{II}}], \tag{64}$$

where S_{I} and S_{II} are the scalar orientational order parameters of sublattices 1 and 2, respectively, and $\psi_{\mathrm{I0}},\psi_{\mathrm{II0}}$ are the angles between the axes of the corresponding tensor order parameters and the axes of the hexagonal lattice. In our Monte Carlo simulations, the angles ψ_{I0} and ψ_{II0} are temperature independent, and therefore the temperature variation of the chiral order parameter is determined by that of the orientational order parameters S_{I} and S_{II} which are presented in Fig. 7. In the ideal infinite phase B, $\psi_{\mathrm{I0}}=-\psi II0=\pi/6$. $S_{\mathrm{I}}=S_{\mathrm{II}}=S$ and the chiral order parameter is proportional to the unique orientational order parameter S,

$$\Delta_B(T)=\tfrac{1}{3}S(T). \tag{65}$$

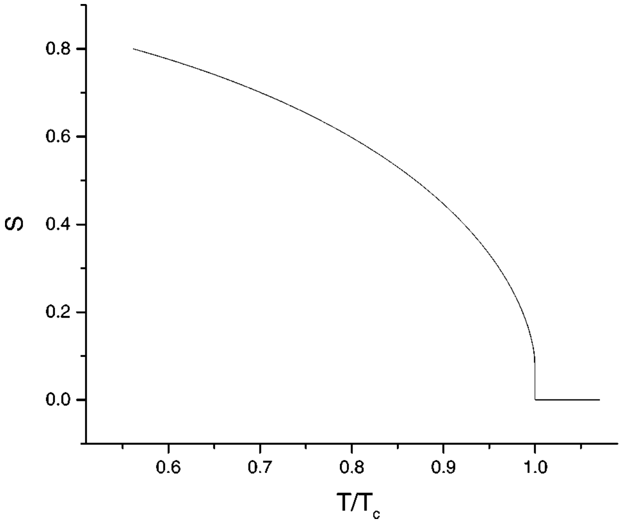

FIG. 11. Temperature variation of the orientational order parameter S of the phase B obtained from Eqs. (53) and (54). The transition temperature $k_BT_c=-(U_++U_-)/2$.

For the mirror image of the phase *B*, the sign in Eq. (65) is reversed. In the framework of the mean-field theory, the orientational order parameter $S(T)$ can be calculated numerically using Eqs. (53) and (54). The temperature variation of *S*, which determined the variation of Δ_B, is presented in Fig. 11. One notes that, in principle, the temperature variation of the order parameter can be determined experimentally by measuring the optical activity on reflection from the monolayer located at the solid-liquid interface.

One can readily see that the chiral order parameter vanishes for the nonchiral phase *C* because in the phase *C*, $\psi_{\mathrm{I}0}=\pi$ and $\psi_{\mathrm{II}0}=0$. Thus the transition into the phase *C* corresponds to a *nonchiral* translational symmetry breaking. As discussed in Sec. IV, in the phase *B* three sublattices rapidly interchange their roles during the course of simulation. For a given sublattice, the angle ψ_0 jumps from $+\pi/6$ to $-\pi/6$ and back, and therefore the chiral order parameter alternates in sign. This means that the initial nonchiral symmetry is restored during the course of simulation.

VI. DISCUSSION

In this paper, we have developed a mean-field theory of the transition between the isotropic phase and the orientationally ordered phase composed of tripod molecules on the flat surface. Such molecules, which are typical building units of thermotropic liquid crystals in the bulk, possess a threefold symmetry axis perpendicular to the flat core. The molecules are assumed to be located on the sites of the two-dimensional hexagonal lattice which has been clearly observed experimentally in the self-assembled monolayers formed by a series of discotic mesogenic molecules on a pyrolithic graphite surface [11]. A simple model potential of interaction between rigid tripod molecules has been derived using only the molecular symmetry and taking into consideration that in the general case, any pair interaction potential for two rigid molecules on the flat surface depends only on two angles which specify the orientation of these molecules with respect to the intermolecular vector. As shown in Sec. III, the simple analytical form of the model potential can be obtained by keeping the first two terms of the general expansion. A similar potential has been used also in the theory of 3D columnar ordering in the system of discotic molecules of the same structure [26].

The model potential (34) is a sum of two terms which represent different kinds of intermolecular interactions. The first term depends only on the angle between the side chains of the two neighboring molecules. This part of the potential is not sensitive to the orientation of the two molecules with respect to the intermolecular vector, and, therefore, it has the same value for all pairs of nearest neighbors on the lattice provided the angle between the side chains of the molecules remains fixed. This term promotes parallel or antiparallel orientation of neighboring tripod molecules depending on the sign of the coupling constant U_-. By contrast, the second term in Eq. (34) does depend on the relative orientation of the two molecules with respect to the intermolecular vector, and thus the corresponding interaction energy may be different for different pairs of nearest neighbors on the lattice. This part of the potential is mainly determined by a short-range steric repulsion between long side chains of neighboring tripod molecules. Such chains may overlap for some particular relative orientations of two neighboring molecules, and the corresponding interaction energy should be strongly positive. This determines the positive sign of the corresponding coupling constant U_+.

In a 2D system of tripod molecules on the hexagonal lattice, the simplest orientational phase transition occurs if the first part of the interaction potential (34) is predominant. In this case, the interaction potential is approximately the same for pairs of nearest neighbors and the system undergoes the second-order transition from the orientationally disordered ("isotropic" if the symmetry of the lattice is ignored) to the orientationally ordered 2D tripod phase [see Fig. 1(a)], which is characterized by the threefold symmetry axis perpendicular to the surface. One notes that this threefold symmetry is lower than the sixfold symmetry of the lattice. The orientational ordering of tripod molecules in such a phase is characterized by the scalar order parameter $S=\langle\cos 3\psi\rangle$ which is determined by the self-consistency equation (48) which is similar to the corresponding equation found in the 2D Maier-Saupe theory [27] that describes the isotropic-nematic phase transition on the surface. At the same time, the tensor order parameter of the tripod phase, discussed in detail in Sec. II, is very much different from the one for the 2D nematic phase. This difference is determined by a difference in point symmetry groups of the two phases. In the 2D nematic phase, there exists only one *nonpolar* direction of ordering of long molecular axes, while in the 2D tripod phase one finds three equivalent *polar* directions specified by three equivalent directors $\mathbf{l}_1$, $\mathbf{l}_2$, and $\mathbf{l}_3$ (see Fig. 2).

The homogeneous tripod phase is expected to be stable when the side chains of the tripod molecules are sufficiently short (i.e., when they are significantly shorter than the lattice period). However, the experimental situation seems to be the opposite [11] and therefore one cannot neglect the second part of the interaction potential, which is determined by a short-range repulsion between side chains.. As shown in Sec. IV, the homogeneous tripod phase is unstable if $U_+>U_-$. In the latter case, there is a frustration in the system because, on one hand, all molecules have a tendency to be parallel or antiparallel (depending on the sign of U_+). On the other hand, there is no such homogeneous orientation of tripod molecules on the lattice which corresponds to a minimum of the total free energy because the side chains of some nearest neighbors will always overlap. The free energy of such system may decrease if the system of tripod molecules on the hexagonal lattice splits into three sublattices which are characterized by different values of the orientational order parameter and different orientations of the director. This means that the system undergoes a phase transition with simultaneous orientational and translational symmetry breaking. A different type of such transition has recently been considered in Ref. [28]. One notes that in the present system, any two nearest neighbors belong to different sublattices. This enables the system to avoid frustration provided different sublattices have different orientations of the director.

As shown in Sec. IV, the actual values of the orientational order parameters for three different sublattices and the corresponding angles which specify the orientations of the three directors can be found by minimization of the total free energy. This minimization procedure is different from the one used in the conventional molecular theory of nematic liquid crystals where the free energy does not depend on the orientation of the director which is assumed to be uniform throughout the system (in the ideal system without boundaries). In such a case, the free energy is minimized only with respect to the scalar nematic order parameter which satisfies a self-consistency equation. By contrast, in the system of tripod molecules considered in this paper, the orientational order parameters of the three sublattices are determined by a system of three equations which depend on the angles between directors in different sublattices. One notes that in the simple mean-field approximation, minimization of the total free energy yields three solutions which correspond to the three phases presented in Fig. 1. The first solution corresponds to the uniform orientationally ordered phase without sublattices, while the second solution describes the ordered phase composed of three sublattices which exactly corresponds to the 2D chiral structure of disklike mesogenic molecules on the graphite substrate, observed in the experiment [11]. In such a phase, one sublattice is orientationally disordered while the two other sublattices are characterized by the same degree of ordering (i.e., the scalar order parameters of the two sublattices are equal) and opposite directions of ordering (i.e., the directors of the two sublattices are antiparallel). In addition, the angle between the directors and a crystallographic axis of the underlying hexagonal lattice exactly corresponds to the experimental findings. This nonzero angle between the direction of ordering and axes of the hexagonal lattice determines the 2D chirality of the tripod phase which does not have any symmetry line within the plane. In this phase, the molecules which belong to the orientationally disordered sublattice are surrounded by six ordered tripod molecules which split into three pairs with antiparallel average orientation. The existence of this phase is mainly determined by short-range repulsion between long chains of neighboring tripod molecules, and the mean-field theory indicates that the phase can be stable only if $U_+ > U_-$. Comparing the stability conditions for the 2D chiral phase and for the simple uniform orientationally ordered phase, one concludes that these two phases cannot be stable simultaneously. This may explain why the homogeneously ordered phase has not been observed in the experiment. The 2D chirality of the phase *B* can be described by the chiral order paramer which is considered in Sec. V. The chiral order parameter possesses opposite signs for the two enantiomeric forms of the phase *B*, and it vanishes identically for the nonchiral phase *C* which is characterized by a nonchiral translational symmetry breaking. The temperature variation of the chiral order parameter is determined by that of the orientational order parameter *S*.

The results of the simple mean-field theory discussed above have been supported by Monte Carlo simulations performed using the same model intermolecular interaction potential. All three orientationally ordered 2D phases, presented in Fig. 1, have been obtained for appropriate values of the coupling constants U_+ and U_-, which have been taken within the stability range for each phase specified by the theory. It is interesting to note that in the phases with a supramolecular structure, the three different sublattices interchange during the course of simulation. This is related to the fact that initially all lattice sites are equivalent and all nearest neighbors interact via the same pair potential. The infinite 2D hexagonal lattice can be split into three equivalent sublattices presented in Fig. 2 by three possible ways. The free energies of these three configurations are the same and therefore all three states of the whole system should be reached during a sufficiently long Monte Carlo run.

In conclusion, we note that it has been possible to derive a simple molecular model of the experimentally observed 2D chiral phase with rather untrivial supramolecular structure. The model is based on a mean-field theory and on a simple interaction potential which has been derived using only the symmetry of a tripod disklike molecule. The same phase has also been obtained in Monte Carlo simulations using the same model interaction potential. This means that the 2D chiral tripod phase observed in Ref. [11] should be rather common and may also be observed with other substances and on other types of surfaces, provided the molecular symmetry remains the same. More experiments are needed to confirm this prediction.

It is interesting to note that a similar phase has been observed in the bulk liquid crystal composed of disklike molecules [6,7]. In this liquid crystal phase, the molecules form columns with the helical intracolumnar structure and the short-range hexagonal positional order of the columns. According to Ref. [7], the intercolumn separation is smaller than the diameter of the disklike molecules with fully extended chains, and therefore the uniform orientationally ordered columnar phase should also be frustrated. As a result, the supramolecular structure is observed in which some columns are characterized by random helical phases of the molecules and are displaced in the vertical direction with respect to the surrounding six columns which are all at the same height and have a single rotational degree of freedom. The analysis of these 2D amd 3D phases raises a question of the relative role of frustration and the positional and orientational ordering. It is not obvious how the frustration will manifest itself in a fluid 2D phase formed by tripod molecules without any lattice structure. In this case, the molecules cannot ‘‘escape into the third dimension’’ to avoid frustration like in the bulk columnar phase. On the other hand, the formation of a regular supramolecular structure is also hardly possible. This problem may be interesting from the fundamental point of view and is currently under investigation.

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