Entropy-Stabilized Smectic *C* Phase in a System of Zigzag-Shaped Molecules

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We report Monte Carlo simulations of a system of rigid zigzag-shaped molecules that demonstrate that simple excluded-volume interactions are sufficient to produce a fluid tilted lamellar [smectic *C* (Sm*C*)] liquid crystal phase. The molecules are composed of three rigidly linked hard spherocylinders arranged in a zigzag fashion. By varying the zigzag angle we have mapped out the whole phase diagram as a function of pressure and zigzag angle Ψ. For Ψ between 35° and 80° our model simulation exhibits the Sm*C* phase. This is the first conclusive evidence where steric interactions arising out of molecular shape alone induce the occurrence of the Sm*C* phase for a wide range of zigzag angles. For smaller Ψ, a transition from tilted crystal to crystal is observed.

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Liquid crystal (LC) phases are very sensitive to the molecular shape. Relating their macroscopic properties to structures of the molecules is a very complex problem. Nevertheless, it is essential to understand this structure-properties relationship both from a fundamental point of view as well as for different technological applications. Computer simulations have emerged as an important tool to investigate the relation of liquid crystal phase behavior to the structure of the constituent molecules. Various models have been used, including simple spherocylinders or hard-sphere chains which interact through hard or soft excluded-volume repulsion [1–3], molecules with ellipsoid shape interacting through Gay-Berne potential [4,5], and simple "bead-spring" representation of molecules interacting through a Lennard-Jones potential [6]. There are also simulations involving atomistic models of real liquid crystal molecules [7–9].

There are a number of theories for the formation of the smectic *C* phase, the phase of two-dimensional fluid layers in which rod-shaped molecules are coherently tilted with respect to the layer planes, based on microscopic models of intermolecular interactions [10–16]. In McMillan theory it is the electric dipole-dipole interactions, which produce tilt in the smectic *C*. Later the quadrupole-quadrupole interaction was introduced as a perturbation of the smectic *A* phase to get a smectic *A* to smectic *C* transition [13,14]. Motivated by the large discrepancy observed between x-ray and the optical data for the molecular tilt angle in smectic *C* materials, Bartolino *et al.* [17], pursuing an idea from Guillon and Skoulios [18], proposed a particular organization of core and tail tilt (known as the zigzag model) derived from lyotropic systems: a rigid optically anisotropic central core tilted to give the tilt of the optical axis and melted aliphatic end chains which are on average less tilted. Real LC molecules are flexible, however, and an astronomical number of distinct molecular conformations are present. Spontaneous symmetry breaking in the Sm*C* phase leads to a collective state in which zigzag-shaped molecular conformations are favored in a statistical sense. Wulf [16], while studying such zigzag-shaped molecules, concluded that the tilted smectic *C* can be formed due to their steric interactions. In this Letter we consider the microscopic origin of the smectic *C* phase. There are also a number of simulations concerning the occurrence of the smectic *C* phase, but none of them are conclusive as to its origin. Neal and Parker have performed simulations of model molecules comprising three rigidly linked Gay-Berne sites arranged in a zigzag fashion [19] but did not find the occurrence of the smectic *C* phase. Evidence of the smectic *C* phase with varying tilt angle from layer to layer was reported in simulation of zigzag-shaped molecules comprising seven rigidly bonded soft spheres [20,21]. In this Letter we consider the microscopic origin of the smectic *C* phase and investigate if steric interaction arising from molecular shape alone can induce tilt in the smectic phase.

The model molecule used here is comprised of three rigidly linked hard spherocylinders of length/breadth ratio L/D arranged in a zigzag configuration (see the inset in Fig. 1). Both ends of the molecule make an angle Ψ with the core. The idea behind using such a hard-core model is that liquid crystal phase behavior is largely entropy driven and determined by the hard-core repulsion between the liquid crystal mesogens. The hard spherocylinder model is convenient both in terms of computational ease and theoretical approach. It has been studied extensively and exhibits a rich phase behavior including isotropic, nematic, smectic *A*, and crystal phases. The advantage of using such a hard-core model is that we can readily vary the shape of the molecule (by changing Ψ) and see how that affects the large-scale organization of the liquid crystal phases. Such a system is athermal; i.e., pressure P is proportional to temperature T and the phase behavior depends only on density and molecular shape.

For convenience we introduce reduced units. The reduced pressure P^* is defined as $P^* = \beta P v_0$ and a reduced

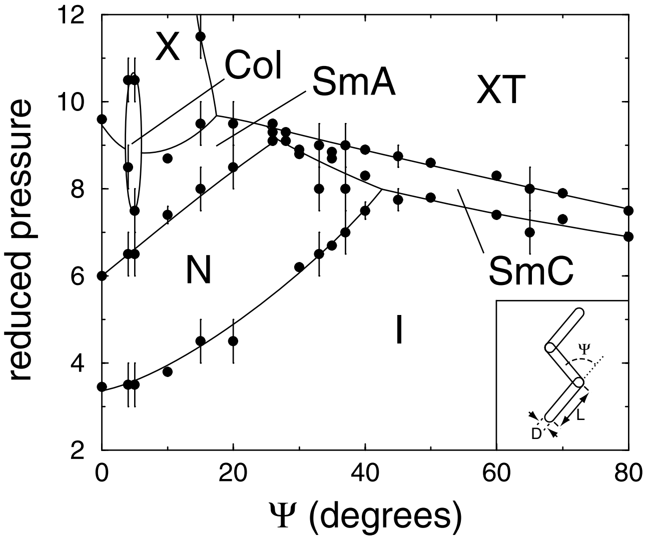

FIG. 1. Phase diagram of zigzag shape molecules with aspect ratio $L/D = 2$ as a function of opening angle Ψ and reduced pressure $P*$. The following phases are present: isotropic liquid (I), nematic (N), smectic A (SmA), smectic C (SmC), columnar (Col), tilted crystal (XT), and crystal (X).

density $\rho^* = \rho v_0$, where v_0 is the volume of the straight hard spherocylinder ($\Psi = 0$) made of three hard spherocylinders of length/breadth ratio L/D. We have performed Monte Carlo (MC) simulation in the N-P-T ensemble with periodic boundary condition on a system of 400 zigzag shaped molecules. The simulation cell consists of $N = 400$ molecules in a cubic box of dimension $L_x \times L_y \times L_z$. For each zigzag angle, the system is initially prepared at high pressure in the close-packed fcc-like crystal phase (antipolar crystal). The unit cell contains two molecules and is defined by the three lattice vectors $\mathbf{a} = D[1/\cos\theta, 0, 0]$, $\mathbf{b} = D[1/(2\cos\theta), \sqrt{3}/2, 0]$, $\mathbf{c} = D[0, 0, 6L/(D\cos\theta) + 2\Delta z]$ with $\Delta z = \sqrt{39\cos^4\theta - 6\cos^2\theta - 1}/(4\sqrt{3}\cos^2\theta)$ and $\theta = \Psi/2$. The positions of the center of mass of the molecules in a unit cell are $\mathbf{r}_1 = D[0, 0, 0]$ and $\mathbf{r}_2 = D[L\sin\theta/D + \Delta x, \Delta y, 3L\cos\theta/D + \Delta z]$ with $\Delta x = 1/(2\cos\theta)$ and $\Delta y = (3\cos^2\theta - 1)/(4\sqrt{3}\cos^2\theta)$. Starting from the crystal phase at high pressure ($P^* = 13$) we decrease the pressure successively by steps of $\Delta P^\star = 1$, until we reach a reduced pressure $P^\star = 1$. For each run, at a given pressure, the final equilibrated configuration obtained from the previous higher pressure is used as the initial state. At each state point ($P^\star, \Psi$) the system is equilibrated for 200 000 MC cycles and 1×10^6 MC cycles are used for the production of the results and the analysis of the various thermodynamical and structural quantities. During each MC step each molecule was chosen randomly and displaced using Metropolis criteria. Reorientation moves were performed using quaternions [22]. In all the simulations reported below, we use a length to breadth ratio $L/D = 2$.

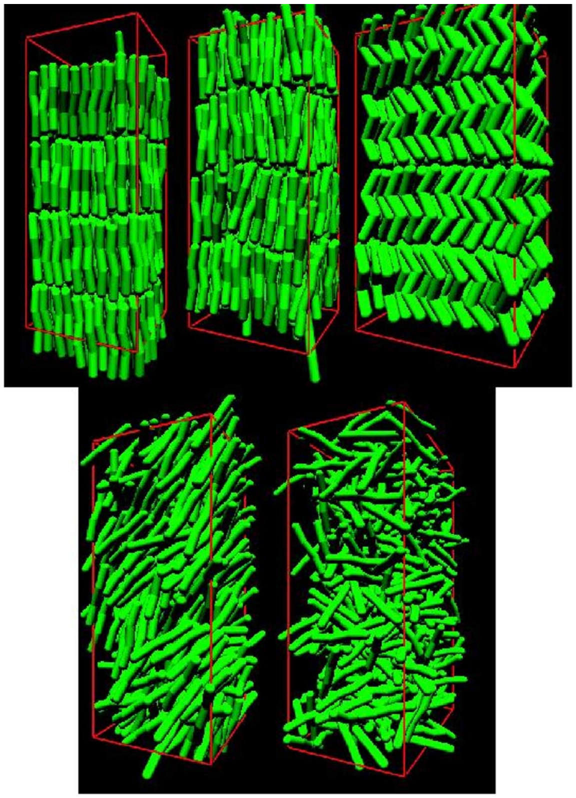

FIG. 2 (color online). Final configurations from Monte Carlo simulations of a system of 400 zigzag molecules for various zigzag angles and pressures. From left to right, top to bottom: crystal ($\Psi = 15°$, $P^\star = 11$); smectic A ($\Psi = 15°$, $P^\star = 9$); smectic C ($\Psi = 65°$, $P^\star = 8$); nematic phase ($\Psi = 15°$, $P^* = 5$); isotropic phase ($\Psi = 15°$, $P^* = 1$).

In order to fully characterize different phases of the system various order parameters were computed. The location of the solid-liquid phase boundary is determined by computing the in-layer translation order parameters $|\rho_{\mathbf{G}k}|^2$, where $\rho_{\mathbf{G}k} = \frac{1}{M}\sum_{j=1}^{M} \exp(i\mathbf{G}_k \cdot \mathbf{r}_j)$. $\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3$ are the reciprocal basis vectors and $\mathbf{r}_j$ is the position of the center of mass of the molecule j, and M is the number of molecules in a given layer.

The smectic-nematic phase boundary is determined by the layer translational order parameter $|\rho_{\parallel}|^2$ with $\rho_{\parallel} = \frac{1}{N}\sum_{j=1}^{N} \exp(i\mathbf{G}_{\parallel} \cdot \mathbf{r}_j)$, where $\mathbf{G}_{\parallel} = \frac{2\pi}{d}\hat{\mathbf{z}}$, the layer normal being along $\hat{\mathbf{z}}$.

To distinguish between a tilted and a nontilted phase (smectic or crystal) we introduce the in-layer smectic C order parameter $|\mathbf{C}|^2$ with $\mathbf{C} = \frac{1}{M}\sum_{j=1}^{M} \hat{\mathbf{c}}_j$. $\hat{\mathbf{c}}_j$ is the projection of the unit vector $\hat{\mathbf{u}}_j$ onto the layer plane, where $\hat{\mathbf{u}}_j$ is defined as the unit vector along the core segment of molecule j, having $\hat{\mathbf{u}}_j \cdot \hat{\mathbf{z}} > 0$.

The orientational order-isotropic phase boundary is determined by the eigenvalues of the second-rank tensorial orientational order parameter $Q_{\alpha\beta}$ defined as $Q_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}(\frac{3}{2}n_{i_\alpha}n_{j_\beta} - \frac{1}{2}\delta_{\alpha\beta})$ with $\alpha, \beta = x, y, z$ and $\mathbf{n}_j$ is the molecular end-to-end unit vector of molecule j. The nematic order parameter S is given by the largest eigenvalue of the ordering tensor $Q_{\alpha\beta}$. The value of S is close to zero in the isotropic phase and will tend to 1 in the highly ordered phase.

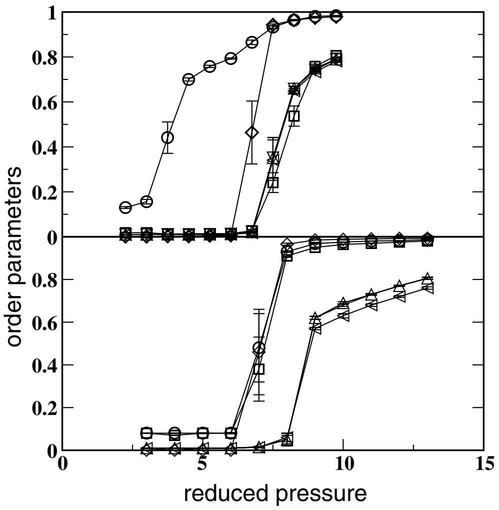

FIG. 3. Evolution of order parameters as a function of reduced pressure for opening angles of $\Psi = 20°$ (top) and $\Psi = 65°$ (bottom) showing, respectively, the phase sequences XT–Sm*A*–N–I and XT–Sm*C*–I as a function of decreasing pressure. The following order parameters are plotted: (△,▽,▷) solid-liquid order parameters $|\rho_1|^2$, $|\rho_2|^2$, $|\rho_3|^2$; (□) smectic *C* order parameter $|\mathbf{C}|^2$; (◇) smectic order parameter $|\rho_{\parallel}|^2$; (○) the largest eigenvalue of the nematic order parameter $Q_{\alpha\beta}$.

To distinguish between Sm*A* and Sm*C* we compute the tilt angle of the central spherocylinder (core) of the zigzag-shaped molecule with the layer normal. We determine the tilt angle θ from the second-rank tensorial orientational order parameter $Q_{\alpha\beta} = (1/N)\sum_{j=1}^{N}(3u_{j\alpha}u_{j\beta} - \delta_{\alpha\beta})/2$, where $\alpha, \beta = x, y, z$, and $\mathbf{u}_j$ is a unit vector along the long axis of central spherocylinder of molecule *j*. The tilt angle is defined as the angle between the largest-eigenvalue eigenvector of the time-averaged ordering tensor $\langle\mathbf{Q}\rangle$ and the layer normal.

To map out the complete phase diagram we have performed simulations for several zigzag angles in between $\Psi = 0°$ and 80°. The phase diagram (Ψ, P^*) is presented in Fig. 1. The system exhibits rich phase behavior with isotropic liquid (I), nematic (N), smectic *A* (Sm*A*), smectic *C* (Sm*C*), columnar (Col), tilted crystal (XT), and crystal (X) phases. Configurations from the isotropic, nematic, smectic *A*, and crystal phases are shown in Fig. 2 for a zigzag angle $\Psi = 15°$. Also shown in the same figure is a configuration from the smectic *C* phase for a zigzag angle $\Psi = 65°$. The phase diagram is completely isomorphous to the phase diagram obtained for bent-core molecules represented as hard-core dimer formed by two interdigitated hard-core spherocylinders sharing one spherical end cap [23]. The Sm*C* replaces the polar Sm*A* phase found in bent-core molecules since polar symmetry breaking leads, for the zigzag model, to a phase having all the symmetries defining a tilted smectic phase. Close-packing interactions combined with the molecular zigzag geometrical shape induce a tilt of the molecules with respect to the layer normal.

The nematic phase is stable for zigzag angles smaller than $\Psi = 40°$. With increasing zigzag angle, the region of stability of the nematic phase decreases, vanishing for $\Psi \geq 40°$, leading to an (I, N, Sm*C*) triple point near $\Psi = 40°$. The existence of a biaxial nematic phase remains an elusive possibility in thermotropic LCs. Zigzag molecules are a good candidate to exhibit a biaxial nematic phase due to their geometrical anisotropy. However, no such phase has been found in our study, confirming the results obtained with bent-core molecules [23]. As is clear from simulations of the hard biaxial ellipsoid system [24,25], a biaxial nematic phase requires a highly biaxial molecular shape. Because such a requirement could be satisfied for larger L/D and specific zigzag angle in the present model, the possibility of the presence of a biaxial phase should not be ruled out.

Because straight spherocylinders do not exhibit any Sm*C* ordering, it is expected that our model should exhibit a transition from Sm*A* to Sm*C*. This transition occurs for a zigzag angle between 26° and 28° and is associated with two triple points, a (Sm*A*, Sm*C*, N) triple point near $\Psi = 28°$ and a (Sm*A*, Sm*C*, XT) triple point near $\Psi = 26°$. Figure 3 displays the evolution of the order parameters for opening angles $\Psi = 20°$ and $\Psi = 65°$. In the latter case, a Sm*C* phase characterized by a high value of both the smectic and tilt order parameters is present while in the former case the appearance of a Sm*A* phase is accompanied by a jump to zero of the tilt order parameter. The Sm*A*–Sm*C* transition is purely entropy driven arising from excluded-volume effects. In Fig. 4 we have plotted the smectic tilt angle as a function of the zigzag angle for $P^* = 8$. The average tilt angle in the middle of the Sm*C* phase is ~10° for $\Psi < 40°$. For $\Psi = 70°$ and 80° the Sm*C* tilt angles are 32° and 48°, respectively. This is the first time that an idealized model system gives conclusive evidence of the occurrence of a Sm*C* phase. Because of the weak tilt coupling between adjacent Sm*C* layers, it proved impossible to determine the relative stability of synclinic (uniform tilt direction in all layers) and anticlinic (alternating tilt direction) ordering by direct simulation. However, it is reasonable to assume that the synclinic state is the thermodynamic ground state of this model, based on our earlier simulation studies of the hard spherocylinder [26] and hard spherocylinder dimer models [23], which demonstrated that the entropy content of anisotropic fluctuations of the interface between adjacent Sm*C* layers provides a general thermodynamic mechanism that uniquely favors synclinic ordering (the "sawtooth" model).

We also find a transition between a tilted crystalline phase and an untilted crystalline phase (i.e., a rotator phase). This rotator phase is stable for zigzag angles smaller than $\Psi = 20°$ and is characterized by a (Sm*A*, X, XT) triple point around $\Psi = 18°$. Quite interestingly, the rotator phase competes with a columnar phase for $3° \leq \Psi \leq 6°$. This narrow columnar phase is characterized by significant two-dimensional

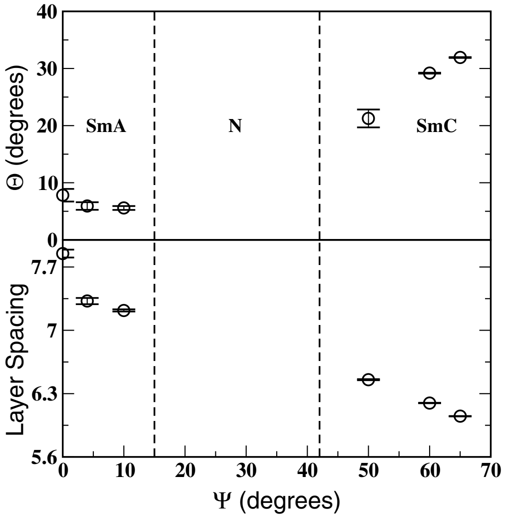

FIG. 4. Tilt angle (θ) (top) and layer spacing (bottom) as a function of the zigzag angle for $P^* = 8$.

crystal order parameters but a negligible smectic order parameter.

Insights into the shape of the phase boundaries can be gained by supposing, to a first approximation, that the partition function of the system can be decomposed into a product of positional and orientational contributions, in which case the entropy is the sum of an orientational entropy and a translational entropy. Competition between different forms of entropy determines the stability of a given phase at a given density. In the limit of straight spherocylinders ($\Psi = 0°$), the isotropic-nematic phase transition occurs when the gain in positional entropy S^{pos} exceeds the loss of orientational entropy S^{orient} [27]. A nematic-smectic phase transition occurs when the gain in translational entropy perpendicular to the long molecular axis $S_{\perp}^{\text{pos}}$ exceeds the loss of positional entropy parallel to the long molecular axis $S_{\parallel}^{\text{pos}}$, leading to the formation of a stack of two-dimensional liquid layers. Similar reasoning can be applied to zigzag molecules: in the range $0° < \Psi < 40°$, the isotropic phase is more favorable at smaller zigzag angles. As the cores become more bent (larger zigzag angles), the gain in positional entropy associated with nematic ordering is reduced, and the nematic phase range is reduced, eventually disappearing for $\Psi > 40°$. The shape of the nematic-SmC boundary (i.e., for $30° < \Psi < 40°$) can be qualitatively understood in the same way by noticing that the positional entropy parallel to the long molecular axis $S_{\parallel}^{\text{pos}}$ is larger for smaller zigzag angles than for larger ones, stabilizing the nematic phase for smaller zigzag angles.

The model exhibits a rich phase behavior including tilted and nontilted crystal, columnar, smectic A, smectic C, nematic, and isotropic phases. The model shows without any ambiguity that excluded-volume interaction arising out of a molecular shape is sufficient to produce the tilted smectic phase even in the absence of electrostatic interactions.

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