Phase Behavior of Bent-Core Molecules

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Recently, a new class of smectic liquid crystal phases (SmCP phases) characterized by the spontaneous formation of macroscopic chiral domains from achiral bent-core molecules has been discovered. We have carried out Monte Carlo simulations of a minimal hard spherocylinder dimer model to investigate the role of excluded volume interactions in determining the phase behavior of bent-core materials and to probe the molecular origins of polar and chiral symmetry breaking. We present the phase diagram as a function of pressure or density and dimer opening angle \( \psi \). With decreasing \( \psi \), a transition from a nonpolar to a polar smectic phase is observed near \( \psi = 167^\circ \), and the nematic phase becomes thermodynamically unstable for \( \psi < 135^\circ \). No chiral smectic or biaxial nematic phases were found.

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Molecular chirality plays an important role in the science of liquid crystals (LCs), leading to cholesteric LCs [1], blue phases [2], ferroelectric [3] and antiferroelectric [4] smectic phases, and twist grain boundary phases [5]. In all of these examples, chirality is an intrinsic property built into the chemical structure of the LC molecules. Recently, a new class of smectic LC phases (SmCP phases) characterized by the spontaneous formation of macroscopic chiral layers from achiral molecules has been discovered [6, 7]. The molecules comprising these phases have ‘bow’ or ‘banana’ shaped cores. The resulting phases exhibit two spontaneous symmetry-breaking instabilities: polar molecular orientational ordering within the layer plane, and molecular tilt, which together produce chiral layers with a handedness that depends on the direction of the tilt relative to the polar axis. Very large second order nonlinear optical (NLO) coefficients have been measured in the ferroelectric state of such materials, bearing some promising applications in NLO devices [8, 9].

From a theoretical point of view, the relationship of phase behavior to the specific bent-core molecular shape is of fundamental interest. In this paper, we investigate a minimal excluded volume model of bent-core mesogens, focusing on the molecular origin of polar and/or chiral symmetry breaking. Of particular interest is the coupling between polar and chiral symmetry breaking. In all bent-core materials studied to date, polar symmetry breaking is accompanied by chiral symmetry breaking induced by molecular tilt. This empirical fact raises the question whether there is a fundamental connection between polarity and chirality in molecular fluids. Another empirical observation is that bent-core materials exhibiting SmCP phases generally do not exhibit nematic phases, although two exceptions have recently been reported [10, 11]. One objective of this study is to establish the molecular shape requirements for the occurrence of the nematic phase in bent-core materials. Finally, we explore the possibility of biaxial nematic ordering in bent-core materials, motivated by recent experimental indications [1, 2].

Hard core models are particularly appealing due to their simplicity and relative ease of computation, both in simulation and theory. In particular, hard spherocylinders have been widely studied as simple models for conventional LCs [13, 14]. This model exhibits rich phase behavior including isotropic, nematic, smectic, columnar and solid phases, the phase transitions being driven by the competition of two main entropic contributions, the orientational entropy favouring the isotropic phase and the positional entropy favouring ordered phases, as shown in the forties by Onsager in the limit of infinitely thin rods [15].

To capture the main characteristics of the collective behavior of bent-core molecules, we extend the spherocylinder model by introducing a hard-core dimer formed by two interdigitated hard-core spherocylinders sharing one spherical end cap (see inset in Figure 1). This is an ideal model system to consider due to the relatively small parameter space. There are three parameters: two geometrical parameters, namely the length-to-breadth ratio \( L/D \), where \( L \) and \( D \) are respectively the length and the diameter of each spherocylinder, and the opening angle \( \psi \) between the two spherocylinder axes; and one thermodynamic parameter, the reduced pressure \( P^* \) defined as \( P^* = \beta P v_o \) or, equivalently, the reduced density \( \rho^* \) defined as \( \rho^* = \rho v_o \). Here, \( v_o \) is the volume of the equivalent straight hard spherocylinder (\( \psi = 180^\circ \)), \( v_o = \pi D^3/6 + \pi L/D^2/4 \) with \( L' = 2L \). In all the simulations presented below, we consider a single value for the length-to-breadth ratio, namely \( L/D = 5 \). This ratio has been chosen in order to roughly represent the equivalent geometrical envelope described by a realistic bow shaped molecule, with fully extended aliphatic tails.

Using a similar model, Camp et al. [16] have found a nematic phase and a smectic A phase of bent-core molecules roughly half as long as the ones considered...
here. However, no systematic study of the phase behavior was carried out. Recently, a polar smectic A phase and a chiral crystal phase have been observed for a ‘polybead’ model of bent-core molecules with an opening angle of $\psi = 140^\circ$ \cite{17}.

To investigate the phase behavior of our model as a function of the pressure and of the opening angle $\psi$, we perform $NPT$ Monte Carlo (MC) simulations, with periodic boundary conditions, on a system of $N = 400$ bent-core molecules. For each opening angle, the system is initially prepared at high pressure in the crystal phase corresponding to the highest number density (antipolar crystal, see Figure 2). The equation of state $P^*(\rho^*)$ is determined by measuring the density $\rho^*$ as the pressure is decreased incrementally from the crystaline state. At each state point ($\psi$, $P^*$), 2 $\times$ $10^5$ MC cycles are used for equilibration and 1 $\times$ $10^6$ MC cycles are used for production of the results.

The location of the phase boundaries is determined from the equation of state $P^*(\rho^*)$, and the nature of the coexisting phases is investigated through the computation of various order parameters. In-layer crystalline order is probed with the translational order parameter $\rho_\parallel$ defined as $\rho_\parallel = \frac{1}{N} \sum_{j=1}^{N} \exp(iG_\parallel \cdot r_j)$ where $G_\parallel$, $G_2$ and $G_\beta$ are the reciprocal basis vector of a deformed hexagonal lattice, $r_j$ is the position of the center of mass of the molecule $j$, and $N$ is the number of molecules in a given layer. The smectic order is measured by the layer translational order parameter $\rho_\parallel$ defined as $\rho_\parallel = \frac{1}{N} \sum_{j=1}^{N} \exp(iG_\parallel \cdot r_j)$ with $G_\parallel = \frac{2\pi}{L/D} \hat{z}$, where $d$ is the layer spacing and $\hat{z}$ is the layer normal. Polar orientational order is detected using the polar order parameter $\mathbf{m}$ defined as $\mathbf{m} = \frac{1}{M} \sum_{j=1}^{M} \hat{m}_j$ where $\hat{m}_j$ is a unit vector contained in the plane of the molecule and passing through the apex of the molecule $[\mathbf{13}]$. Finally, molecular orientational order is determined from the largest eigenvalue of the second-rank tensorial orientational order parameter $Q_{\alpha\beta}$, defined as $Q_{\alpha\beta} = \frac{1}{N} \sum_{j=1}^{N} \left( \frac{1}{2} n_{\alpha j} n_{j\beta} - \frac{1}{2} \delta_{\alpha\beta} \right)$, where $\alpha, \beta = x, y, z$, and $\hat{n}_j$ is a unit vector parallel to the molecular end-to-end vector for molecule $j$.

The $\langle \psi, P^* \rangle$ and $\langle \psi, \rho^* \rangle$ phase diagrams are presented in Figure 1. Rich phase behavior is found, with isotropic (I), nematic (N), smectic A (SmA), polar smectic A (SmAP), columnar (Col), crystal (X) and polar crystal (XP) phases. Configurations from the isotropic, nematic, polar smectic and polar crystalline phases are shown in Figure 2, for an opening angle of $\psi = 165^\circ$.

The nematic phase is stable for opening angles larger than $\psi = 135^\circ$. With decreasing opening angle, the region of stability of the nematic phase decreases, vanishing for opening angles smaller than $\sim 135^\circ$, leading to an (I, N, SmAP) triple point near $\psi = 135^\circ$. It is interesting to note that for dimers half as long as ours, small opening angles seem to destabilize the smectic phase rather than the nematic phase [13].

The vast majority of bent-core materials exhibiting liquid crystal behavior, and in particular SmCP phases, have an opening angle between 120° and 135°, and do not exhibit any nematic phase. Quite interestingly, two classes of bent-core compounds having an opening angle between 134° and 148° [14, 19] exhibit both smectic and nematic phases. These observations, in good qualitative agreement with the predictions of the model, tend to confirm the hypothesis that excluded volume interactions play a central role in the behavior of such materials.

The existence of a biaxial nematic phase remains an elusive possibility in thermotropic LCs. Due to their bent-core geometry, banana molecules are good candidates to investigate such phenomena. Recent experiments suggest that the nematic phase exhibited by two classes of bent-core material might be biaxial [14, 20].

FIG. 1: Phase diagram of spherocylinder dimers (inset) with aspect ratio $L/D = 5$ as a function of opening angle $\psi$ and reduced pressure $P^*$ (top) and reduced density $\rho^*$ (bottom). All two-phase regions are shaded. The following phases are present: isotropic liquid (I), nematic (N), polar smectic A (SmAP), smectic A (SmA), columnar (Col), polar crystal (XP) and crystal (X).
However, the nematic phase presented by our hard-core model does not exhibit any biaxiality. It is likely that the reported biaxiality is due to more subtle interactions and/or to the presence of the flexible tails. A biaxial nematic phase has been reported for hard spherocylinder dimers twice as long as the ones used in the present study, but no transition from/to an isotropic liquid has been reported [16]. Using a simplification of the Onsager second-virial treatment and bifurcation analysis, Teixeira et al. have found a biaxial nematic phase in the limit of very long bent-core molecules [20].

Because straight spherocylinders do not exhibit any polar smectic ordering, it is expected that our model should exhibit a transition from nonpolar smectic (SmA) to polar smectic (SmAP). This transition occurs for an opening angle between 167° and 169°, and is associated with two triple points, a (SmA, SmAP, N) triple point near ψ = 167° and a (SmA, SmAP, XP) triple point near ψ = 169°. Very recently, the first group of bent-core molecules exhibiting both SmCP and a SmA (as well as SmC and nematic phases in one case) have been synthesized [14, 21]. The opening angles measured by NMR techniques for the region of appearance of the smectic A remains in the range of 132° to 145° but no polar order has been detected [22], lowering the upper limit of stability of a polar smectic phase with respect to our predictions.

Figure 3 displays the evolution of the order parameters for opening angles ψ = 157.5° and ψ = 172.5°. In the former case, a polar smectic phase characterized by a high value of both the smectic and polar order parameters is present while in the later case the appearance of a smectic phase from the higher density crystal phase is accompanied by a jump to zero of both the crystal order parameters and the polar order parameter. The smectic phases (both polar and nonpolar) do not exhibit any tilt. Nevertheless, our results tend to confirm the hypothesis that the polar ordering is related to the distinctive bent-core shape of the molecules but is not strongly related to the molecular tilt. Thus, polarity does not imply chirality.

A transition between a polar crystalline phase and a narrow nonpolar crystalline phase (i.e a rotator phase) is also present. This rotator phase is stable for opening angles larger than ψ = 172.5°, and is characterized by a (SmA, X, XP) triple point around ψ = 172.5°. Quite interestingly, the rotator phase competes with a columnar phase for opening angles larger than ψ = 174° and smaller than ψ = 180°. This narrow columnar phase is characterized by a significant crystal order parameters but a negligible magnitude of the smectic order parameter. Since no evidence of such a phase was found for straight spherocylinders, a slightly bent molecular shape seems to favor the appearence and the stabilization of a columnar phase. Due to the rather unexpected appearance of the columnar phase, we performed additional
studies of this region of the phase diagram using helical periodic boundary conditions \[2\] for \( N = 400 \) and a direct ‘quench’ from a crystalline state to the middle of the columnar phase for \( \psi = 176^\circ \) with helical periodic conditions for a larger system (\( N = 1600 \)). A columnar phase was observed in both studies. However, we feel that free energy computations are needed in order to assess the relative thermodynamic stability of the columnar phase, the nonpolar smectic phase, and the rotator phase.

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 a 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, the isotropic–nematic phase transition occurs when the gain in positional entropy \( S_{\text{pos}} \) exceeds the loss of orientational entropy \( S_{\text{orient}} \). A nematic–smectic phase transition occurs when the gain in translational entropy perpendicular to the long molecular axis \( S_{\parallel} \) exceeds the loss of positional entropy parallel to the long molecular axis \( S_{\perp} \), leading to the formation of a stack of two-dimensional liquid layers. Similar reasoning can be applied to bent-core molecules: in the range \( 134^\circ < \psi < 180^\circ \), the isotropic phase is more favourable at smaller opening angles. As the cores become more bent, the gain in positional entropy associated with nematic ordering is reduced. The nematic phase range is then reduced, eventually disappearing for \( \psi < 134^\circ \). The shape of the nematic–SmAP boundary (i.e., for \( 134^\circ < \psi < 167^\circ \)) can be qualitatively understood in the same way by noticing that the positional entropy parallel to the long molecular axis \( S_{\parallel} \) is larger for larger opening angles than for smaller ones, stabilizing the nematic phase for larger opening angles. This trend is reversed for the nematic–SmA transition (i.e., for \( \psi > 167^\circ \)) because the absence of polar order leads to jamming, reducing the translational entropy perpendicular to the long molecular axis \( S_{\perp} \) for decreasing opening angles. This effect is responsible for the enhanced stability of the nematic phase for decreasing opening angles.

The spherocylinder dimer model exhibits rich phase behavior, including polar and nonpolar crystal, columnar, polar and nonpolar smectic, nematic and isotropic phases. In particular the existence and range of stability of the nematic phase is in good agreement with the behavior of the new class of bent-core molecules, while the stability of the nonpolar smectic A phase is in qualitative agreement with experiments. In addition our model predicts the existence and stability of a polar smectic A phase for \( \psi < 167^\circ \). Such phases remain to be found. No tilted phases are exhibited by the model, and a simple extension of the present model, taking into account the important steric role played by the flexible LC tails in the formation of tilted smectic phases, is currently under investigation. Our model indicates that there is no intrinsic coupling between polar symmetry breaking and chiral symmetry breaking, and that the later is not directly related to the bent-core shape of the molecules.

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