Entropy driven formation of Smectic C in system of Zig-zag shaped molecules

Prabal K. Maiti\textsuperscript{1,}\textsuperscript{*}, Yves Lansac\textsuperscript{1,}\textsuperscript{*}, Matthew A. Glaser and Noel A. Clark

\textit{Ferroelectric Liquid Crystal Material Research Center, Department of Physics, University of Colorado, Boulder, CO 80309}

We have carried out Monte Carlo simulations of zig-zag shaped molecules where the the molecules is composed of three rigidly linked hard spherocylinder arranged in a zigzag fashion. By varying zigzag angle we have mapped out the whole phase diagram as a function of pressure, molecular density and zigzag angle $\Psi$. For $\Psi$ between 35$^\circ$ and 80$^\circ$ our model simulation exhibits SmC phase. This is the first conclusive evidence where steric interaction arising out of molecular shape alone induce the occurrence of SmC phase for a wide range of zigzag angle. For smaller $\Psi$, a transition from tilted crystal (XT) to crystal is observed.

PACS numbers: 61.30.-v, 61.30.Cz

Liquid crystal phase is very sensitive to the molecular shape. Relating the macroscopic properties of liquid crystal phase to the microscopic structures of the molecules is very complex problem. On the other hand it is essential to understand this structure-properties relationship both from fundamental point of view as well as for different technological applications. Theoretically it is a very difficult task since it involves hundreds of molecules and their mutual interactions. Computer simulations has emerged as an important tool to investigate the dependence of the liquid crystal phase behavior to the structure of the constituent molecules. Various models has been used such as simple spherocylinder or hard-sphere chains which interact through hard or soft excluded-volume repulsion \cite{2,3,4}, molecules with ellipsoid shape interacting through Gay-Berne potential \cite{5,6}, simple "bead-spring" representation of molecules interacting through Lennard-Jones potential \cite{7,8}. There are also simulations involving atomic level models of real liquid crystal molecules \cite{7,8}.

There are a number of theoretical works which gives a microscopic theories for the formation of smectic C phase \cite{17,18,19,20,21,22}. In McMillan theory it is the electric dipole-dipole interactions which produce tilt in the smectic C. Later quadrupole-quadrupole interaction was introduced as a perturbation of smectic A phase to get a smectic C transition \cite{20}. 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. \cite{18}, resuming an idea from Guillon and Skoulios \cite{14}, proposed a molecular model (known as the zigzag model) derived from lyotropic systems: the rigid central core, optically anisotropic, imposes the tilt of the optical axis and the melted aliphatic end chains are on average closer to the normal to the layers. Wulf \cite{22} while studying the zigzag shaped molecules concluded that the tilted smectic C is formed due to the steric interactions arising out of the packing arrangement of such molecules. There are number of simulations concerning the occurrence of smectic C phase, but none of them are conclusive of model molecules comprising three rigidly linked Gay-Berne (GB) sites arranged in a zigzag fashion \cite{19} and but did not find the occurrence of smectic C phase. Evidence of 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 \cite{11}. One of the major goal of this paper is to investigate if steric interaction arising from molecular shape alone can induce tilt in the smectic phase.

The model molecule is comprised of three rigidly linked hard spherocylinders of length/breadth ratio $L_{rod}/D$ arranged in a zigzag configuration (see the inset in figure 1). Both ends of the molecule is making an angle $\Psi$ with the core. The idea behind using such 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. Hard spherocylinder provides a simple model both in terms of computational ease and theoretical approach. It has been studied extensively and exhibit a rich phase behavior including isotropic, nematic, smectic A, and crystal phases. The advantage of using such hard core model is that we can vary the shape of the molecule (by changing $\Psi$) and see how that affects the large-scale organization of the liquid crystal phases.

For convenience we introduce reduced units. The reduced pressure $P^*$ is defined as $P^* = \beta P v_{hsc}$ and a reduced density $\rho^* = \rho v_{hsc}$, where $v_{hsc}$ is the volume of the straight hard spherocylinder of length $L$ and breadth $D$. We have performed MC simulation in $NPT$ 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 $L_x \times L_y \times L_z$. Initially the system was prepared in a crystal phase at high pressure. Among the possible different crystalline order, we choose the antipolar crystal ordering corresponding to the highest packing density to ensure the highest stability. Starting from crystal phase at high pressure ($P^* = 13$) we decrease the pressure successively by steps of $\Delta P^* = 1$, until we reach a reduced pressure $P^* = 1$. For each run, at a given pres-
from the previous higher pressure is used as the initial state. At each state point \((P^*, \Psi)\) the system is equilibrated for 200000 MC cycles and one million 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 molecules were chosen randomly and displaced using Metropolis criteria. The reorientation move was performed using quaternion \([23]\). In all the simulations reported below, we use a length to breadth ratio \(L_{ban}/D = 2\).

In order to fully characterize different phases of the systems various order parameters were computed. The location of the solid–liquid phase boundary is determined by computing the squared-magnitude of the in-layer translation order parameter \(S\) is given by the largest eigenvalue of the ordering tensor

\[
\rho_{G_k} = \frac{1}{M} \sum_{j=1}^{M} \exp(iG_k \cdot r_j) \tag{1}
\]

\(G_1, G_2, G_3\) are the reciprocal basis vectors and \(r_j\) 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 squared-magnitude of the layer translational order parameter \(\rho_{||}\) defined as

\[
\rho_{||} = \frac{1}{N} \sum_{j=1}^{N} \exp(iG_{||} \cdot r_j) \tag{2}
\]

where \(G_{||} = \frac{2\pi}{\Psi} \hat{z}\), the layer normal being along \(\hat{z}\).

To distinguish between a tilted and a non tilted phase (smectic or crystal) we introduce the in-layer polar order parameter \(\hat{m}\) defined as

\[
\hat{m} = \frac{1}{M} \sum_{j=1}^{M} \hat{m}_j \tag{3}
\]

where \(\hat{m}_j\) is the unit vector contained in the plane of the molecule and passing through one of the apex of the molecule. With this definition, care must be taken to ensure that two zigzag molecules having the z-component of the end-to-end vector pointing in opposite direction have in fact the same polar direction.

The orientational order–isotropic phase boundary is determined by the eigenvalues of the second-rank tensorial orientational order parameter \(Q_{\alpha\beta}\) defined as

\[
Q_{\alpha\beta} = \frac{1}{N} \sum_{j=1}^{N} \left( \frac{3}{2} a_{\alpha j} n_{\beta j} - \frac{1}{2} \delta_{\alpha\beta} \right) \tag{4}
\]

with \(\alpha, \beta = x, y, z\) and \(n_j\) is the molecular end-to-end unit vector of molecule \(j\). The nematic order parameter \(S\) is given by the largest eigenvalue of

\[
\begin{pmatrix}
\frac{3}{2} a_{xx} & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & \frac{3}{2} a_{yy} & \frac{1}{2} \\
\frac{1}{2} & \frac{1}{2} & \frac{3}{2} a_{zz}
\end{pmatrix}
\]

zero in the isotropic phase and will tend to one in highly ordered phase.

To distinguish between SmA and SmC we compute the tilt angle of the central spherocylinder (core) of the zigzag shaped molecule with the layer normal.

To map out the complete phase diagram we have performed simulations for several zig-zag angles in between \(\Psi = 0\) and \(80^\circ\). The phase diagram \((\Psi, P^*)\) is presented in Fig. 1.

The system exhibits rich phase behavior with isotropic liquid (I), nematic (N), smectic A (SmA), smectic C (SmC), columnar (Col), tilted crystal (XT), crystal (X) phases. Configurations from the isotropic, nematic, smectic A and tilted crystal phases are shown in Fig. 2 for a zigzag angle \(\Psi = 15^\circ\). Also shown on the same figure a configuration from the smectic C phase for a zigzag angle \(\Psi = 65^\circ\). 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 \([24]\). The SmC replaces the polar SmA (SmAP) 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-packging interactions combined to 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 \(\Psi = 40^\circ\). With increasing zigzag angle, the region of stability of the nematic phase decreases, vanishing for zigzag angles larger than \(\sim 40^\circ\), leading to an (I, N, SmC) triple point near \(\Psi = 40^\circ\). The existence of a biaxial nematic phase remains an elusive possibility in thermotropic LCs. Zigzag molecules are good candidate to exhibit biaxial nematic due to their geometrical phase.
FIG. 2: Final configurations from Monte Carlo simulations of \( N = 400 \) zigzag molecules as a function of pressure. From left to right, top to bottom: crystal (\( \Psi = 15^\circ, P^* = 11 \)), smectic A (\( \Psi = 15^\circ, P^* = 9 \)), smectic C (\( \Psi = 65^\circ, P^* = 8 \)), nematic phase (\( \Psi = 15^\circ, P^* = 5 \)), isotropic phase (\( \Psi = 15^\circ, P^* = 1 \)).

study, confirming the results obtained with bent-core molecules [24]. As is clear from simulations of the hard biaxial ellipsoid system [25, 26], 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 SmC ordering, it is expected that our model should exhibit a transition from SmA to SmC. This transition occurs for a zigzag angle between 26° and 28°, and is associated with two triple points, a (SmA, SmC, N) triple point near \( \Psi = 28^\circ \) and a (SmA, SmC, XT) triple point near \( \Psi = 26^\circ \). The SmA–SmC transition is purely entropy driven and arise from packing effect. In figure 3 we have plotted the smectic tilt angle (defined as the average over the tilt angle with respect to the layer normal made by the central spherocylinder of every molecules) as a function of the zigzag angle. This is the first time that an idealized model system gives conclusive evidence of the occurrence of a SmC phase. Due to the weak coupling between adjacent layers in the SmC phase, it was impossible to determine the relative stability of synclinic (a uniform tilt direction in all layers) and antclinic order by direct simulations. But it is reasonable to assume that the zigzag model obeys the same general thermodynamic mechanism like the hard spherocylinder and the hard-dimer models that we have recently studied [9, 24]. In these studies within a framework of "sawtooth" model, we have demonstrated that the entropy content of molecular-scale fluctuations of the interface between smectic C layers ("out-of-layer" molecular fluctuations) provides a general thermodynamic mechanism that uniquely favors synclinic ordering.

We also find a transition between a tilted crystalline phase and a untitled crystalline phase (i.e a rotator phase). This rotator phase is stable for zigzag angles smaller than \( \Psi = 20^\circ \), and is characterized by a (SmA, X, XT) triple point around \( \Psi = 18^\circ \). Quite interestingly, the rotator phase competes with a columnar phase for zigzag angles larger than \( \Psi \sim 3^\circ \) and smaller than \( \Psi \sim 6^\circ \). This narrow columnar phase is characterized by significant two-dimensional crystal order parameters but a negligible magnitude of the 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
different forms of entropy determines the stability of a given phase at a given density. In the limit of straight spherocylinders ($\Psi = 0^{\circ}$), the isotropic–nematic phase transition occurs when the gain in positional entropy $S^{pos}_{\parallel}$ exceeds the loss of orientational entropy $S^{orient}_{\parallel}$. A nematic–smectic phase transition occurs when the gain in translational entropy perpendicular to the long molecular axis $S^{pos}_{\perp}$ exceeds the loss of positional entropy $S^{pos}_{\parallel}$, leading to the formation of a stack of two-dimensional liquid layers. Similar reasoning can be applied to zig-zag molecules: in the range $0^{\circ} < \Psi < 40^{\circ}$, the isotropic phase is more favourable 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 $\Psi > 40^{\circ}$. The shape of the nematic–SmC boundary (i.e., for $30^{\circ} < \Psi < 40^{\circ}$) can be qualitatively understood in the same way by noticing that the positional entropy parallel to the long molecular axis $S^{pos}_{\parallel}$ 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 molecular shape is sufficient to produce tilted smectic phase even in the absence of electrostatic interactions.

This work was supported by NSF MRSEC Grant DMR 98-09555.

1. Present address: Materials and Process Simulation Center, 139-74 California Institute of Technology, Pasadena, CA 91125, U.S.A.
* Email : maiti@wag.caltech.edu.
! Email : lansac@wag.caltech.edu.

[1] P. G. de Gennes and J. Prost, in The Physics of Liquid Crystals, 2nd ed. (Oxford University Press, New York, 1993).
[2] S. C. McGrother, D. C. Williamson, and G. Jackson, J. Chem. Phys. 104, 6755 (1996).
[3] P. Bolhuis and D. Frenkel, J. Chem. Phys. 106, 666 (1997).
[4] D. C. Williamson and G. Jackson, J. Chem. Phys., 108, 10294 (1998).
[5] J. G. Gay and B. J. Berne, J. Chem. Phys. 74, 3316 (1981).
[6] M. A. Bates and G. R. Luckhurst, J. Chem. Phys., 110, 7087 (1999).
[7] M. R. Wilson and M. P. Allen, Mol. Cryst. Liq. Cryst., 198, 465 (1991)
[8] M. A. Glaser, R. Malzbender, N. A. Clark, and D. M. Walba, J. Phys.: Condens. Matter, 6, A261 (1994).
[9] M. A. Glaser and N. A. Clark, Phy. Rev. E., 66, 021711 (2002).
[10] F. Affouard, M. Kröger and S. Hess, Phys. Rev. E., 54, 5178 (1996).
[11] J. Xu, R. L. B. Selinger, J. V. Selinger, B. R. Ratna and R. Shashidar, Phys. Rev. E., 60, 5584 (1999).
[12] M. P. Neal, A. J. Parker and C. M. Care, Mol. Phys., 91, 603 (1997).
[13] R. Bartolino, J. Doucet and G. Durand, Ann. Phys., 3, 389 (1978)
[14] D. Guillou and A. Skoulos, J. Physique (Paris), 38, 79 (1977).
[15] I. M. Withers, C. M. Care and D. J. Cleaver, 113, 5078 (2000).
[16] J. Xu, R. L. B. Selinger, J. V. Selinger and R. Shashidar (preprint).
[17] W. L. McMillan, Phys. Rev. A11, 365 (1974).
[18] D. Cabib and L. Benguigui, J. Phys. (Paris) 38, 419 (1977).
[19] B. W. van der Meer and G. Vertogen, J. Phys. (Paris), Colloq. 40, C3-222 (1979).
[20] W. J. A. Goossens, Europhys. Lett., 3, 341 (1987).
[21] E. Velasco, L. Mederos, and T. J. Sluckin, Liq. Cryst., 20, 399 (1996).
[22] A. Wulf, Phys. Rev. A11, 365 (1975).
[23] M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids, (Oxford, 1987).
[24] Y. Lansac, P. K. Maiti, N. A. Clark, and M. A. Glaser, Phys. Rev. E., 67, 011703 (2003).
[25] M. P. Allen, Liq. Cryst. 8, 499 (1990).
[26] P. J. Camp, M. P. Allen, J. Chem. Phys. 106, 6681 (1997).
[27] L. Onsager, Ann. (N. Y.) Acad. Sci. 51, 627 (1949).