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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Transitions of Bowlic Liquid Crystals

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Version of record first published: 13 Dec 2006.

To cite this article: K. M. Leung & Lin Lei (1987): Phase Transitions of Bowlic Liquid Crystals, Molecular Crystals and Liquid Crystals, 146:1, 71-76

To link to this article: http://dx.doi.org/10.1080/00268948708071803

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Mol. Cryst. Liq. Cryst., 1987, Vol. 146, pp. 71–76
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Phase Transitions of Bowlic Liquid Crystals†

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(*Received July 15, 1986*)

The isotropic to nematic transition in bowlic liquid cyrstals are theoretically examined with the help of the work by Krieger and James on a molecular crystal model. In addition to the conventional non-polar nematic phase, a polar nematic phase can also exist. The polar nematic–isotropic and the polar nematic–nonpolar nematic transitions can be either first or second order, and two tricritical points as well as one triple point exist (while the nonpolar nematic–isotropic transition is always first order).

Keywords: bowlic liquid crystal, nematic–isotropic transition

I. INTRODUCTION

A new type of liquid crystal consisting of a rigid bowl-like central core surrounded by symmetrically located flexible side chains was theoretically predicted,[1] and very recently synthesized and studied experimentally.[2–4] X-ray diffraction[2,4] and optical[3] studies showed

†Presented at the 11th International Liquid Crystal Conference, Berkeley, June 30–July 4, 1986.

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that the molecules tend to stack on top of one another and form well ordered columnar mesophases. The transition between columnar and isotropic phase seems to be first order.[2-4] There is as yet no complete theoretical work reported on the possible mesophases[1] and the kind of transitions that these bowlic liquid crystals can have.

As pointed out by Lin (see also Ref. 5), the macroscopic symmetry of the director, $\hat{n} \rightarrow -\hat{n}$, which is valid as a rule in mesophases of both rod-like and disc-like molecules, may be violated owing to the up-down asymmetry of the bowl-like central core and the steric effects associated with the geometry of these bowlic molecules. We will investigate some of the possible effects associated with this asymmetry, and the possible resulting mesophases of this new and exciting type of liquid crystals.

We want to consider in particular the isotropic to nematic transition in these liquid crystals. Although bowlic-nematics have not yet been seen, there is no *apriori* reason to preclude their existence, however. Recall that in the case of the discotic liquid crystals, it takes two years after the discotic columnar phases have been observed,[6] before the discovery of discotic nematics.[7] Guided by making analogue with discotic nematics, one can expect bowlic nematics to be found in bowlic molecules in which the ratio between the length of the side chains and the size of the central core[7,8,9] is small.

II. INTERMOLECULAR POTENTIAL

An important consequence due to the loss in the up-down symmetry is that a dipolar type interaction between bowlic molecules cannot, in principle, be ruled out. In addition, the side chains in these molecules can be substituted by polar homologues, and thus the molecules can acquire a net electric dipole moment along the C_3 symmetry axis of the molecule. We will discuss the possible consequences of this type of interaction on the isotropic to nematic transition.

Since we are only interested here in the isotropic to nematic transition, a Maier-Saupe[10] type of model that neglects the positional degrees of freedom is appropriate. We let $\hat{\Omega}_i = (\theta_i, \phi_i)$, where θ_i and ϕ_i are, respectively the polar and the azimuthal angles of the central axis of the molecule with respect to a fixed spatial frame.

For axially symmetrical molecules, we let the intermolecular potential to be given by

$$V_{ij} = -V_1 P_1 (\cos \theta_{ij}) - V_2 P_2 (\cos \theta_{ij}) \qquad (1)$$

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where $\theta_{ij} \equiv \cos^{-1}(\hat{\Omega}_i \cdot \hat{\Omega}_j)$ is the angle between the central axes of the ith and the jth molecules. Note that the V_1 term, which represents a dipolar type interaction, is absent from the conventional Maier-Saupe theory of rod-like liquid crystals.

It must be emphasized that, although such a term has been discussed, even for rod-like molecules, by a number of authors, especially Chandrasekhar,[11-12] and the predictions based on the model in (1) have been confirmed in certain experiments,[13-14] there are two important differences. First, V_1 was taken in their work to be negative (in our present notation), therefore assuming that the molecules would prefer an anti-ferroelectric alignment. In contrast, we expect that V_1 should be positive here for the bowl-like molecules, implying that these molecules would prefer a parallel rather than anti-parallel alignment with adjacent molecules, as illustrated in Figure 1. Our choice is suggested by experimental observations that the bowl-like molecules tend to stack on top of one another, especially in the columnar phase.[2-4] In particular, in the case where the central core of these molecules is made of cyclotriveratrylene, the molecules stack into columns even in the crystalline phase.

Second, no long range ferro- or anti-ferroelectric order was assumed in their calculation, i.e. $\langle P_1(\cos\theta)\rangle = 0$, this is consistent with the experimental facts for rod-like or disc-like liquid crystals. Besides the usual long ranged orientational order with $\langle P_2(\cos\theta)\rangle \neq 0$, only a short range anti-ferroelectric order was assumed. However for the

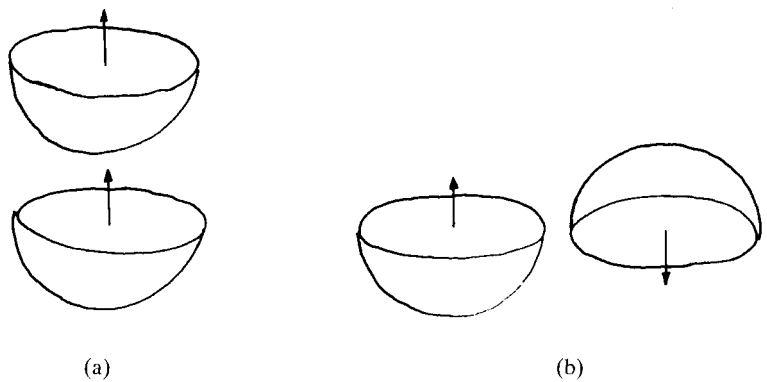

FIGURE 1 For two adjacent bowlic molecules, the parallel configuration (a) is preferred over the anti-parallel configuration (b). For the purpose of illustration, we arbitrarily pick the electric moment to point in the direction towards the open end of the molecule.

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bowl-like molecules here, this is not necessarily the case. Polar-nematics may form which has long range ferroelectric order.

In addition to the V_1 term, there is the usual V_2 term with V_2 positive. As a result of this term, a parallel or antiparallel configuration with adjacent molecules is favored. Thus in this work we will adopt the model in (1) with both V_1 and V_2 positive.

III. MEAN FIELD PREDICTIONS

It turns out that Krieger and James[15] have made a detailed mean field study of this model some time ago. Although their work was primarily intended for molecular crystals, and a discrete lattice was assumed, their results can be borrowed to describe the isotropic to nematic transition in bowl-like liquid crystals.

Besides the usual orientational order parameter, $Q = \langle P_2(\cos\theta)\rangle$, there is also a polar order parameter, $P = \langle P_1(\cos\theta)\rangle$, which describe the possible existence of ferroelectricity. Noting that we must replace their Az by $-V_1$, and Bz by $-V_2$, the mean field phase diagram is shown in Figure 2.

One can see that from the isotropic phase with $P = Q = 0$, the bowl-like liquid crystal can transform into two different nematic phases, a non-polar nematic phase with $P = 0$ and $Q \neq 0$, and a polar nematic phase with $P \neq 0$ and $Q \neq 0$. The non-polar nematic phase is similar to the conventional nematic phase in rod-like and disc-like nematics, where there is no long range ferroelectric order, but a finite orientational order. The polar nematic phase, however, has a finite orientational order as well as a finite spontaneous ferroelectric order. Clearly it is physically impossible to have $P \neq 0$ while at the same time $Q = 0$. The phase diagram as well as the order of the transition are shown in Figure 2. We see that there are two tri-critical points and one triple point, where the isotropic, non-polar and polar nematic phase can co-exist. This triple point is at a temperature T_3 given by $kT_3/V_2 = 0.2202$. The second order line which separates the non-polar from the polar nematic phase in fact goes to zero as V_2/V_1 goes to infinity. Thus at low temperatures where T is less than T_3 and if the V_1 interaction is not very strong, then the more conventional non-polar nematics is favored.

IV. CONCLUSIONS AND DISCUSSIONS

The polar-nematic phase of the bowl-like liquid crystal described here should be very interesting in its own right. We should also point out

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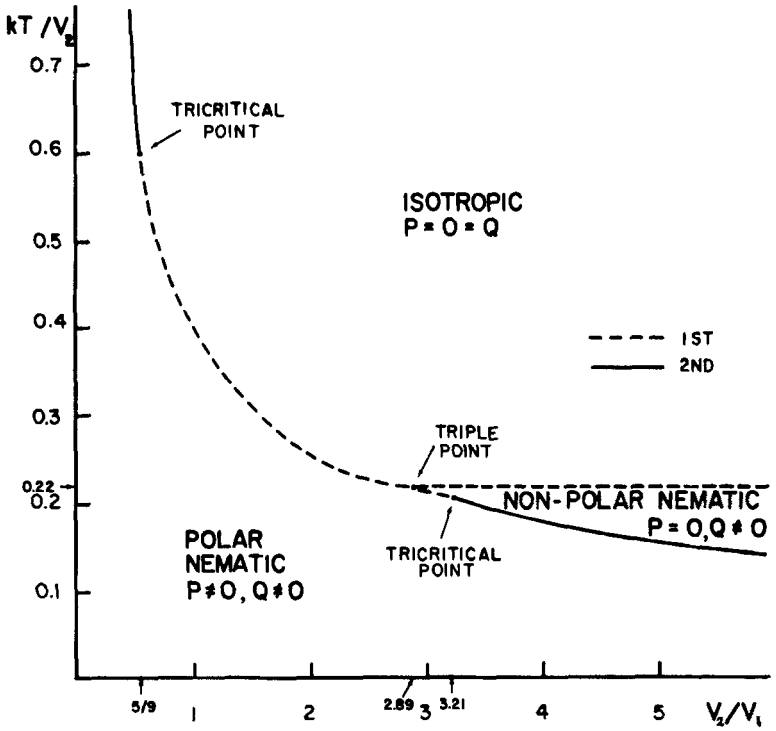

FIGURE 2 The isotropic to nematic phase diagram in the bowlic liquid crystals, as adapted from the mean field calculation of Krieger and James.[15] First (second) order lines are marked by dashed (solid) curves. k is the Boltzman constant.

that liquid crystals commonly exhibit sizable nonlinear optical effects. However, owing to the usual up-down symmetry of the more conventional liquid crystals, only third and higher odd orders of nonlinear optical phenomena can exist. Even order optical effects, such as second harmonic generation do not occur. With the up-down symmetry possibly broken in these bowl-like liquid crystals, the even order optical effect may now be possible.

We hope that future experiments will be conducted to test the predictions here on the isotropic to nematic transition. In future work, we intend to include the position degrees of freedom, so that the transition from the isotropic phase to the columnar phase, as well as the transformation between the rectangular and hexagonal arrays of two dimensional columns[4] can be studied.

We also like to point out a recent theoretical work by Lee and Grinstein,[16] who found falf-integer and string excitations besides the usual integer vortices in a classical two dimensional XY model. They

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also mentioned that a physical realization of their model is the isotropic to nematic transition of liquid crystals with distinguishable heads and tails in two dimension. It is of interest to see if the bowl-like liquid crystals may provide a system to test their theory.

Finally we want to mention the numerical work developed by Dowell,[17] which may be adapted to investigate some of the transitions described here.

Acknowledgments

We thank H. Zimmermann for valuable discussions. This work is partially supported by a grant from City University of New York PSC-CUNY Research Award Program.

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