Biaxial Nematic Phase in Model Bent-Core Systems

Piotr Grzybowski and Lech Longa
Marian Smoluchowski Institute of Physics, Department of Statistical Physics and Mark Kac Center for Complex Systems Research, Jagellonian University, Reymonta 4, Kraków, Poland

(Received 28 September 2010; revised manuscript received 5 May 2011; published 6 July 2011)

We determine the bifurcation phase diagrams with isotropic (I), uniaxial (N_U) and biaxial (N_B) nematic phases for model bent-core mesogens using Onsager-type theory. The molecules comprise two or three Gay-Berne interacting ellipsoids of uniaxial and biaxial shape and a transverse central dipole. The Landau point is found to turn into an I-N_B line for the three-center model with a large dipole moment. For the biaxial ellipsoids, a line of Landau points is observed even in the absence of the dipoles.

DOI: 10.1103/PhysRevLett.107.027802 PACS numbers: 64.70.M−, 61.30.Cz, 61.30.Eb

In 1970 Freiser [1] predicted that long and flat molecules could form a biaxial nematic phase of D_{2h} symmetry, in addition to the N_U phase. While lyotropic [2] and polymeric [3] biaxial phases were indeed found, a low molecular weight, thermotropic N_B phase, proved to be extremely difficult to stabilize [4]. It was not until 2004 that Madsen *et al.* [5] and Acharya *et al.* [6] announced that bent-core molecules, also often referred to as V shaped, may form the elusive N_B phase. Their molecules consist of two relatively rigid mesogenic groups linked together through a central unit with the angle $\gamma \approx 140°$ between the two groups. Such molecules are clearly biaxial and exhibit a near-C_{2v} symmetry. They also contain a large transverse dipole moment ($\sim$ 4D). Other thermotropic systems for which N_B has also been reported are V-shaped molecules with $\gamma \approx 90°$ [7] and organosiloxane tetrapodes [8,9]. Unexpectedly, the results of recent investigations show that proof of the long-range biaxial order can be more challenging than earlier thought [10–12]. It seems the kind of consistency one would hope for from different experimental methods is lacking.

The issue of stable N_B phase for V-shaped systems has also been addressed at the level of statistical mechanics [13–16]. With the aid of Onsager theory, Teixeira *et al.* [13] predicted that molecules composed of two hard spherocylinders joined at their ends can stabilize N_B. In addition, they found a direct I-N_B phase transition at an isolated Landau point [16] for $\gamma \approx 107.36°$. Subsequently, Luckhurst [14] has argued that only within approximately two degrees of the Landau point, the N_B phase would appear above the freezing point of a real uniaxial nematic. Such a narrow range does not cover the experimentally observed apex angles for which N_B was claimed.

Simulations of bent-core molecules have either found no sign of N_B for Gay-Berne (GB) models [17–20], or discovered it only on cooling [21]. In the atomistic approach, a weak biaxiality was proved for compounds from [5,6].

An important step towards better understanding the true nature of the observed nematic order would then be to look systematically into more realistic molecular models where all characteristic features of V-shaped molecules are taken *simultaneously* into account. Although the essential ordering mechanism is expected to be associated, as for ordinary nematics, with entropic interactions we believe that a credible theory should treat dispersion and dipolar interactions on an equal footing with steric repulsion. With this in mind we construct a large class of molecular models for V-shaped molecules and determine the corresponding phase diagrams by finding I-(N_U)-N_B bifurcation diagrams [22,23] from density functional theory (DFT). We study the model molecules constructed out of two- and three-GB sites as shown in Fig. 1. Uniaxial [24] and biaxial [25] GB models are used for intercenter potential energy; the summary of their parameters is given in Table I. In addition, we introduce the dipole moments parallel to the molecular C_{2v} symmetry axis and investigate the influence of the dipole strength on the stability of N_B.

We employ standard GB (dimensionless) reduced units by setting $\sigma_0 = \epsilon_0 = 1$ for the GB potential parameters [24]. We also choose the ratio of length to width of 5:1 for the uniaxial arms to stay close to experimental values. In the case of biaxial GB arms the ellipsoids are oriented such that the shortest axes are perpendicular to the molecular symmetry plane and the longest one is lying in that plane. Those parameters and orientation of the ellipsoids make the attractive forces strongest in the face-to-face configuration [25].

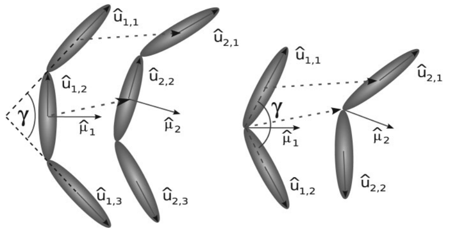

FIG. 1. The construction of V shaped molecules out of two and three firmly attached GB parts. Each part of one molecule interacts with every part from other molecules via $V_{\rm GB}$. Dipole-dipole interaction, $V_{\rm DD}$, is also added.

TABLE I. Intersegment potential model parameters.

Uniaxial GB parameters[24]	$(\nu, \mu) = (1, 2)$, $\kappa = 5$, $\chi' = 1/3$
Biaxial GB parameters [25]	$(\sigma_x, \sigma_y, \sigma_z) = (1.2, 0.514, 3.4)$, $\sigma_c = \sigma_y$
	$(\epsilon_x, \epsilon_y, \epsilon_z) = (1.0, 1.4, 0.2)$, $(\nu, \mu) = (3, 1)$

The resulting GB potential, V_{GB}, for a pair of bent-core molecules is then a sum of four terms for the two-center case and of nine terms for the three-center case. The dipole-dipole part, V_{DD}, is of standard form. The total pair interaction, V, is the sum of V_{GB} and V_{DD}. In Fig. 2 we show the exemplary equipotential surfaces for four different molecular orientations and dimensionless reduced dipole moments μ. The relative importance of the V_{GB} and V_{DD} parts is measured by the ratio $|\frac{V_{\mathrm{DD}}}{V_{\mathrm{GB}}+V_{\mathrm{DD}}}|$, which for $1.2 \leq \mu \leq 2.8$ can be approximated by the quadratic function: $-0.04\mu^2 + 0.39\mu - 0.26$. Assuming that a molecule's arm cross section $\sigma_0 \approx 5$ Å and an energy scale $\epsilon_0 k_B \approx 100$ K, $\mu \approx 2$ should be less than 3D.

We study the equilibrium properties of the systems using the second virial approximation for the direct pair correlation function (DPCF) and restrict ourselves to nematics of $D_{\infty h}$ and D_{2h} symmetry. By minimizing the grand potential with respect to the one-particle distribution function [22,23] the necessary condition for stationary distribution $P(\mathbf{\Omega})$ is given by a self-consistent integral equation. It reads [23]

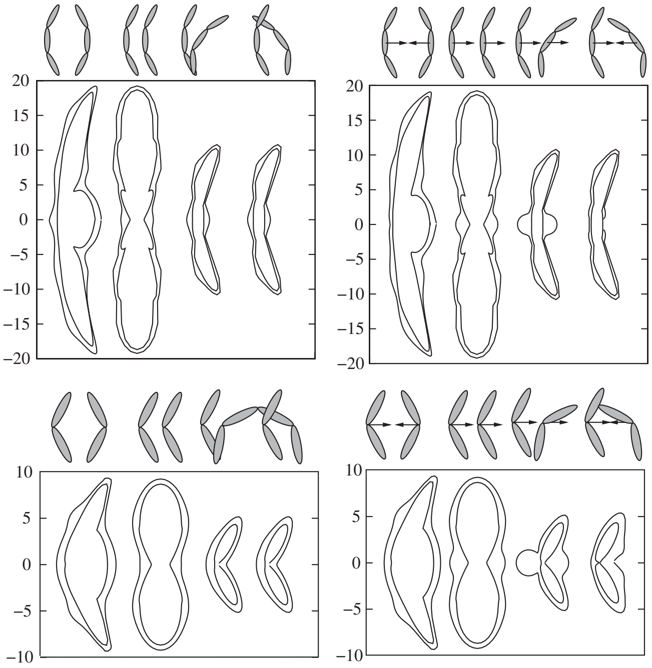

FIG. 2. Exemplary equipotential surfaces for model bent-core molecules composed of 2 (bottom) and 3 (top) uniaxial parts for an arm's elongation of 5:1 and for opening angle $\gamma = 126°$. The case with the dipole-dipole interaction included ($\mu = 2.0$) is shown to the right. Surfaces are shown for the total pair potential equal to 0 and -0.2.

$$P(\mathbf{\Omega}_1) = Z^{-1} \exp\left[\rho \int c_2(\mathbf{\Omega}_1\mathbf{\Omega}_2)P(\mathbf{\Omega}_2)d\mathbf{\Omega}_2\right], \qquad (1)$$

with DPCF: $c_2(\mathbf{\Omega}_1\mathbf{\Omega}_2) = \int\{\exp[-\frac{1}{t}V(\mathbf{\Omega}_1^{-1}\mathbf{\Omega}_2, \mathbf{r}_{12})] - 1\}d^3\mathbf{r}_{12}$ and the normalization constant $Z = \int \exp \times [\rho \int c_2(\mathbf{\Omega}_1\mathbf{\Omega}_2)P(\mathbf{\Omega}_1)d\mathbf{\Omega}_1]d\mathbf{\Omega}_2$; $d\mathbf{\Omega} = d\alpha d(\cos(\beta))d\gamma$ stands for integration over Euler angles parameterizing molecular orientations, $d^3\mathbf{r} = r^2 dr d(\cos(\theta))d\phi$, $\mathbf{\Omega}_1^{-1}\mathbf{\Omega}_2$ is the relative orientation of the molecules, $\rho = \frac{\langle N \rangle}{V}\sigma_0^3$ is the dimensionless reduced density and t temperature. The theory, Eq. (1) is known to stay in reasonable agreement with available simulation data for isotropic and uniaxial nematic phases of GB molecules (see, e.g., [26]).

The expansion of $P(\mathbf{\Omega})$ in the basis of D_{2h} symmetry adapted Δ functions [22]: $P(\mathbf{\Omega}) = \sum_{L,m,n} \frac{2L+1}{8\pi^2} \times \bar{\Delta}_{m,n}^{(L)} \Delta_{m,n}^{(L)}(\mathbf{\Omega})$ allows us to introduce the order parameters $\bar{\Delta}_{m,n}^{(L)} = \int d\mathbf{\Omega} P(\mathbf{\Omega}) \Delta_{m,n}^{(L)}(\mathbf{\Omega})$ for nematics. If, in addition, we expand c_2: $c_2(\mathbf{\Omega}_1\mathbf{\Omega}_2) = \sum_{L,m,n} c_{Lmn} \Delta_{m,n}^{(L)}(\mathbf{\Omega}_1^{-1}\mathbf{\Omega}_2)$, where $c_{Lmn} = \frac{2L+1}{8\pi^2} \int d\mathbf{\Omega}_1^{-1}\mathbf{\Omega}_2 c_2(\mathbf{\Omega}_1\mathbf{\Omega}_2) \Delta_{m,n}^{(L)}(\mathbf{\Omega}_1^{-1}\mathbf{\Omega}_2)$ and where $c_{Lmn} = c_{Lnm}$ due to particle interchange symmetry, then Eq. (1) becomes reduced to a set of nonlinear equations for the order parameters [23]. Using bifurcation analysis we now seek a subset of nonzero order parameters, describing low-symmetry phase, that branch off from the background high-symmetry phase. Generally, in the isotropic phase all order parameters vanish. The uniaxial phase with the director along the z axis is characterized by nonzero order parameters indexed by $m = 0$. Finally, in the biaxial nematic phase all the order parameters become nonzero.

The bifurcation points so determined are either spinodal points for the first-order phase transitions or critical points for the continuous transitions. Hence, for continuous and weakly first-order phase transitions, as holds for isotropic and nematic phases, we arrive at quite accurate estimates of the phase diagrams in the temperature-density plane [27]. Following the analysis as described in [22,23] two different bifurcation formulas can be derived. The first one is the equation for the bifurcation from the isotropic phase to N_U and N_B phases. It reads

$$10/\rho = c_{00} + c_{22} - \sqrt{4c_{02}^2 + (c_{00} - c_{22})^2}, \qquad (2)$$

where $c_{mn} \equiv c_{2mn}$. The bifurcating phase is assigned N_B if no (meta-)stable N_U phase has been detected at the bifurcation point [27]. Interestingly, along the I-N_B line the self-dual condition [23], $c_{22} \approx c_{00} - 2c_{02}/\sqrt{3}$, holds up to assumed numerical accuracy indicating that the I-N_B transition is continuous or very weakly first order. For the

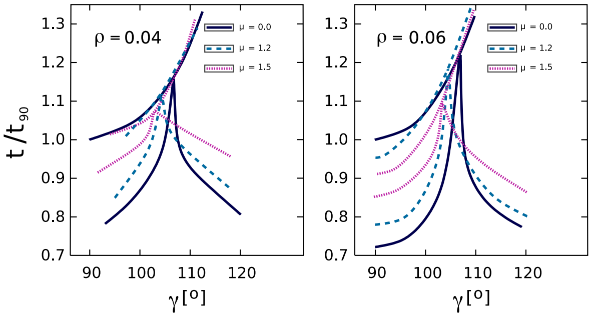

FIG. 3 (color online). Diagrams for a two-part banana shaped molecule, for two densities (ρ) and three values of dipole moment (μ). On each plot two branches of bifurcation from uniaxial to biaxial phase meet the upper line of bifurcations from the isotropic phase at the Landau point ($t = k_B T$).

uniaxial-to-biaxial bifurcation we follow the mean-field procedure and drop c_{Lmn} of $L > 2$. This yields [23]

$$\rho = \frac{35}{\overline{ac}}\Big[2c_{00}(adc_{02} - d) + c_{02}(2a + abc_{22}) - d^2 c_{00} + bc_{22} - \sqrt{a^2 c_{00} c_{22} + bd(c_{00}c_{22} - 2c_{02}^2)}\Big], \tag{3}$$

where $\overline{ac} = (a^2 + 2bd)(c_{02}^2 + c_{00}c_{22})$, $a = 20\bar{\Delta}_{0,2}^{(2)} + \sqrt{15}\bar{\Delta}_{0,2}^{(4)}$, $b = 14 + 20\bar{\Delta}_{0,0}^{(2)} + \bar{\Delta}_{0,0}^{(4)} + \sqrt{35}\bar{\Delta}_{0,4}^{(4)}$, $d = 7 - 10\bar{\Delta}_{0,0}^{(2)} + 3\bar{\Delta}_{0,0}^{(4)}$, and where $\bar{\Delta}_{m,n}^{(L)}$ are determined in the uniaxial nematic phase. Since the formulas for $\bar{\Delta}_{m,n}^{(L)}$'s depend on ρ and t, the Eq. (3) for given t becomes a self-consistent equation for density. Each c_{mn} is a six dimensional integral. The integration procedure incorporated both Monte Carlo and adaptive multipoint Gauss quadratures with relative error kept below 1%.

The bifurcation phase diagrams, which follow from the solutions of the Eqs. (2) and (3) for the uniaxial V_{GB} are shown in Figs. 3 and 4. The results are presented for two densities such that the corresponding packing fraction is of the order of 0.3–0.4. t divided by t_{90} (Table II) is plotted, where t_{90} is the temperature of bifurcation from isotropic phase for $\gamma = 90°$ in the nonpolar case.

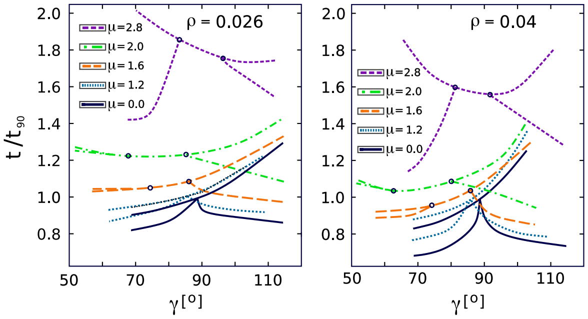

FIG. 4 (color online). Diagrams for a three-part banana shaped molecule, for two densities and five dipole magnitudes. Each plot shows the bifurcation from isotropic phase and two lower branches of uniaxial-to-biaxial phase transition ($t = k_B T$).

TABLE II. Bifurcation temperatures from isotropic phase for $\gamma = 90°$.

ρ	t_{90}
Two-GB molecule:	
0.04	0.84
0.06	0.96
Three-GB molecule:	
0.026	1.34
0.04	1.71

The phase sequence involves the isotropic phase, the rodlike (N_{U+}) and disclike (N_{U-}) uniaxial nematic phase, and the biaxial nematic phase. In the case of a two-part molecule without the dipole moment the Landau point is found for $\gamma \approx 107°$, in agreement with the hard-boomerang model [13]. The diagrams include two dipole strengths of $\mu = 1.2$ and $\mu = 1.5$. The Landau point shifts towards lower angles with increasing μ.

For the nonpolar three-part molecule, the Landau point is found to be at $\gamma = 89°$ and shifting to lower angles with increasing dipole magnitude (Table III, Fig. 5) up to a point where the dipole-dipole interactions make up 20% ($\mu = 1.4$) of the total energy. Above that value the Landau point changes into an I-N_B line that widens with increasing μ; for $\mu = 1.6$ it covers the range of 12° and for $\mu = 2.0$ it extends for more than 20°. The high γ boundary practically does not change (for lower density) and is equal to 86° for $\mu \leq 2.1$. Then the Landau region begins to shrink and shifts towards higher angles. For the largest dipole studied ($\mu = 2.8$) V_{DD} constitutes 50% of the total energy. As can be seen from Fig. 4 the Landau line in that case is still getting shorter and moves towards higher apex angles. Table III shows the evolution of the Landau region as a function of μ. The results are presented for two densities such that the corresponding packing fraction is of the order of 0.3–0.4. As can be seen some differences appear by varying density for the strongest dipoles ($\mu \geq 2.0$). Namely the line of the direct isotropic-biaxial

TABLE III. Landau point versus dipole magnitude μ.

μ	Landau point	
Two-GB molecule:		
0.0	107°	
1.2	104°	
1.5	103°	
Three-GB molecule:		
	$\rho = 0.026$	$\rho = 0.04$
0.0	89°	89°
1.2	86°	86°
1.6	74°–86°	74°–86°
2.0	63°–86°	63°–83°
2.8	83°–97°	82°–92°
Biaxial-GB molecule:		
0.0	121°–128°	

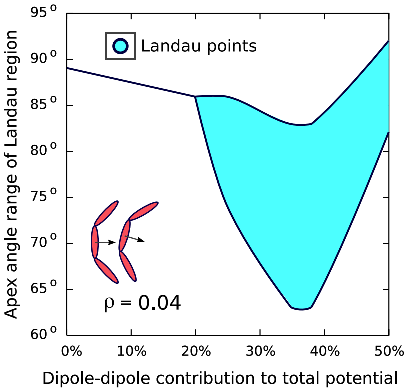

FIG. 5 (color online). Range of direct isotropic-biaxial transitions in apex angle, vs dipole-dipole contribution in the total potential.

transitions shrinks for higher density. Interestingly, the stability region of the uniaxial nematic shrinks with increasing dipole moment, making the biaxial phase more likely to appear away from the Landau point. The last observation holds for both two- and three-part molecules.

Finally, we take into account the model where the GB arms of the molecules are biaxial. The Landau point in the biaxial case, Fig. 6, is replaced by a line of Landau points even for the nonpolar molecule. That line starts near 121° and ends for $\gamma = 128°$. The region becomes reduced to a single point when decreasing the arm's biaxiality.

Summarizing, we have presented DFT bifurcation phase diagrams for a large class of models with features characteristic of a bent-core molecule. Nonpolar models with uniaxial arms revealed a single Landau point, in agreement with results for hard molecules [13]. Inclusion of the dipole-dipole interactions resulted in shifting the Landau point towards lower apex angles for the case of a two-arm molecule. For the three-part molecules a line of direct I-N_B transitions has emerged for large nonzero dipole moments. An optimal dipole range has been predicted that makes the appearance of the biaxial phase most probable. It is worth noting that for all models considered the strengthening of the dipole-dipole interaction resulted in shrinking the distance between the isotropic phase and the biaxial nematic phase, i.e., destabilizing the N_U phase. Thus our studies indicate that an "optimal bent-core molecule" for detecting N_B should consist of two cores that introduce bending in two places along the molecule and an overall transverse dipole of the order of 3D. Finally, the inclusion of biaxial GB ellipsoids as building blocks revealed the direct I-N_B transition line even in the nonpolar, two-arms model. It seems that the only important effect not taken into account in the present studies is molecular flexibility [15,28].

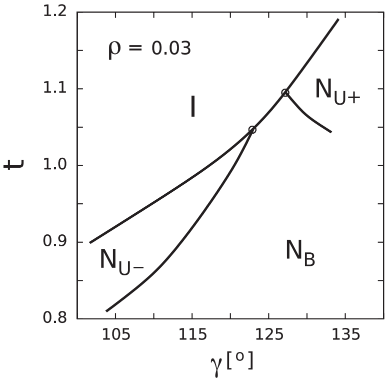

FIG. 6. Bifurcation diagram for nonpolar bent-core molecules modeled by two biaxial GB ellipsoids [25].

This work has been supported by the MNiSW Grant No N202 169 31/3455, ICM Grant No. G27-8, and by the International PhD Programme MPD/2009/6. We thank Dr. P. F. Góra and Dr. M. Cieśla for useful discussions.

[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[3] K. Severing and K. Saalwachter, Phys. Rev. Lett. **92**, 125501 (2004).
[4] G. R. Luckhurst, Nature (London) **430**, 413 (2004).
[5] L. A. Madsen *et al.*, Phys. Rev. Lett. **92**, 145505 (2004).
[6] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
[7] M. Lehmann *et al.*, J. Mater. Chem. **16**, 4326 (2006).
[8] K. Merkel *et al.*, Phys. Rev. Lett. **93**, 237801 (2004).
[9] K. Neupane *et al.*, Phys. Rev. Lett. **97**, 207802 (2006).
[10] K. Van Le *et al.*, Phys. Rev. E **79**, 030701(R) (2009).
[11] M. Nagaraj *et al.*, Appl. Phys. Lett. **96**, 011106 (2010).
[12] M. S. Park *et al.*, Phys. Rev. Lett. **105**, 027801 (2010).
[13] P. I. C. Teixeira, A. J. Masters, and B. M. Mulder, Mol. Cryst. Liq. Cryst. **323**, 167 (1998).
[14] G. R. Luckhurst, Thin Solid Films **393**, 40 (2001).
[15] L. Longa, G. Pająk, and T. Wydro, Phys. Rev. E **76**, 011703 (2007).
[16] D. Allender and L. Longa, Phys. Rev. E **78**, 011704 (2008).
[17] S. J. Johnston, R. J. Low, and M. P. Neal, Phys. Rev. E **66**, 061702 (2002).
[18] S. J. Johnston, R. J. Low, and M. P. Neal, Phys. Rev. E **65**, 051706 (2002).
[19] R. Memmer, Liq. Cryst. **29**, 483 (2002).
[20] S. Orlandi *et al.*, J. Chem. Phys. **124**, 124907 (2006).
[21] W. Józefowicz and L. Longa, arXiv:0904.0666v1.
[22] B. Mulder, Phys. Rev. A **39**, 360 (1989).
[23] L. Longa *et al.*, Phys. Rev. E **71**, 051714 (2005).
[24] J. G. Gay and B. J. Berne, J. Chem. Phys. **74**, 3316 (1981).
[25] R. Berardi, C. Fava, and C. Zannoni, Chem. Phys. Lett. **236**, 462 (1995).
[26] V. V. Ginzburg, M. A. Glaser, and N. A. Clark, Liq. Cryst. **21**, 265 (1996).
[27] P. Grzybowski, Ph.D. thesis, Jagellonian University, 2008 [arXiv:0907.1044v1].
[28] M. A. Bates, Phys. Rev. E **74**, 061702 (2006).