BIAXIAL DISCOTIC GAY-BERNE MESOGENS AND BIAXIAL NEMATICS

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We investigate the thermotropic liquid crystal phases formed in a system of biaxial discotic mesogenic Gay-Berne particles with strong in-plane interactions when the attractive and repulsive biaxialities have the same or the opposite sign. We find that a biaxial nematic phase is obtained when the shape and well depth anisotropies have the same sign while we do not observe a columnar phase.

INTRODUCTION

The discovery of discotic mesogens by Chandrasekhar and collaborators [1] has opened a wide field of research, dramatically showing the importance of molecular shape in determining the type of the phases obtained [1,2]. By now nematics and a variety of columnar phases formed by discotic molecules have been found and studied experimentally [3]. On the computational side discotic mesogens can be modelled, e.g., with oblate attractive – repulsive Gay-Berne (GB) ellipsoids [4,5] with thickness s_f and diameter s_e and nematic and

columnar phases have been simulated, although not as many studies as for calamitic systems are available as yet [6]. It has been shown [7] that a GB model with shape anisotropy $s_f/s_e = 0.345$, face-face to side-side well depth ratio $e_f/e_e = 5$ and GB parameters (see [4]) $m = 1$, $n = 2$ gives an isotropic, nematic and columnar phase with rectangular structure. The simulations of a GB system with the same aspect ratio and attraction anisotropy, but with a parameterisation $m = 1$, $n = 3$ has the effect of lowering the well depths of the face-to-face and side-by-side configurations giving an hexagonal columnar structure [8,9], as often found in real discotic systems. A hexagonal non interdigitated columnar phase was also found with another slightly modified version of the GB potential [10].

However, although discs correspond to a simple limiting case of the actual shape of mesogenic molecules, most molecules, even when we can approximate them with rigid objects, will actually have a lower, e.g. biaxial symmetry. A biaxial nematic phase, where molecules tend to align not only their symmetry axis, but also to stack and align their other axes might then be expected. A biaxial nematic has indeed been theoretically predicted, at least with approximate mean field type theories over thirty years ago [11] and has been found in lyotropics [12] but to date, the proposed thermotropic phases (see, e.g. [13,14] and references therein) are still not universally accepted, based in particular on some contrary deuterium NMR evidence [15].

The first important feature for a good candidate biaxial mesogen to possess is certainly shape and to a first approximation a biaxial molecule can be treated as an ellipsoid with different semi-axis s_x, s_y, s_z, with an attendant shape biaxiality l_σ:

$$\lambda_\sigma = \sqrt{\tfrac{3}{2}}\,(\sigma_x - \sigma_y)/(2\sigma_z - \sigma_x - \sigma_y) \qquad (1)$$

An attempt can then be made to increase l_σ towards the maximum value $1/\sqrt{6}$ beyond which a distorted rod becomes a distorted disc. Optimizing the shape is useful since, as shown by molecular dynamics simulations by Allen [16], a system of hard biaxial ellipsoids can generate a biaxial nematic phase. On the other hand in a real thermotropic the potential biaxial phase can only exist in competition with the formation of a smectic or crystal phase, that in turn can also be favoured by the same change in shape, and it is thus estimated that only a very small biaxiality window exist [17], explaining at least in part the difficulty in obtaining biaxial nematics.

Given the need to fine tune molecular features it is certainly worth considering a biaxial attractive –repulsive potential and generalized GB potentials have been put forward [18]. The introduction of attractive forces offers more possibilities for optimizing the molecular features so as to obtain a good candidate to give nematic phase biaxiality. For an attractive - repulsive potential we can in fact have different well depths $e_x,\ e_y,\ e_z$ for molecules approaching from different directions. These can clearly be treated independently of shape and thus we cannot really talk of a unique biaxiality parameter for a molecule, but we should consider also an attractive biaxiality derived from the relative values of the potential well depths.

In a previous work [19] we have shown, using Monte Carlo computer simulations, that a suitable combination of anisotropies in repulsive and attractive interactions can disfavour the formation of face-face stacked smectics or crystals, thus helping the formation of biaxial nematics. In that case the molecules considered were elongated, with $s_x,\ s_y < s_z.$ To

the best of our knowledge attractive-repulsive biaxial discotics ($s_x, s_y > s_z$) have not yet been studied, and here we wish to provide a first investigation in this direction, examining in particular the type of phases that can be obtained, and the possibility of forming biaxial nematic and columnar organizations.

In the following sections we describe the model employed and the simulations performed and we then concentrate on the results.

MODEL AND SIMULATIONS

We consider a system of biaxial disc-like ellipsoidal particles interacting through a generalized Gay-Berne potential [18]. The Gay-Berne term is a sum of pairwise repulsive and attractive contribution with a 12-6 inverse distance dependence form:

$$U(\omega_1, \omega_2, \mathbf{r}_{12}) = 4\epsilon_0 \epsilon(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$$
$$\times \left[\left(\frac{\sigma_c}{r_{12} - \sigma(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) + \sigma_c} \right)^{12} \right.$$
$$\left. - \left(\frac{\sigma_c}{r_{12} - \sigma(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) + \sigma_c} \right)^{6} \right]. \quad (2)$$

with strength, e, and range, s, parameters dependent on the orientations w_1, w_2 of the two particles and on their separation vector $\mathbf{r}$ (the cap indicates a unit vector) as discussed in [18]. We employ the same parameterization introduced by us in [8] for the GB exponential

coefficients, using $m= 1$, $n= 3$. For such a biaxial GB particle the attractive biaxiality mentioned in the Introduction can be defined as:

$$\lambda_\epsilon = \sqrt{\tfrac{3}{2}}\,(\epsilon_x^{-1/\mu} - \epsilon_y^{-1/\mu})/(2\epsilon_z^{-1/\mu} - \epsilon_x^{-1/\mu} - \epsilon_y^{-1/\mu}) \qquad (3)$$
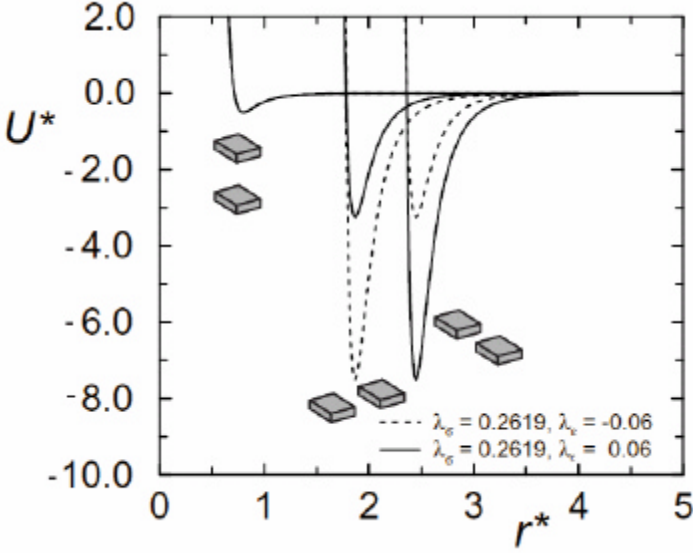

FIGURE 1 Gay-Berne potential for biaxial discotic mesogens with shape parameters $s_x=1.780$, $s_y=2.360$, $s_z=0.714$, well depths $e_x=1.80$, $e_y=0.78$, $e_z=0.12$ ($l_\epsilon=-0.06$) or $e_x=0.78$, $e_y=1.80$, $e_z=0.12$ ($l_\epsilon=0.06$) and parameters $m=1$, $n=3$ as a function of intermolecular separations $r^*=r/s_0$.

We have seen in [19] an example of biaxial GB potential with biaxialities of opposite sign. Choosing a negative l_ϵ had in that case the effect of energetically disfavouring face to face configurations and proved very useful in actually obtaining a thermotropic nematic biaxial

phase in our MC simulations [19]. In this work we have simulated a system of N=1024 GB particles with s_x=1.780, s_y=2.360, s_z= 0.714 and well depths e_x= 0.78, e_y= 1.80, e_z= 0.12 or respectively e_x=1.80, e_y= 0.78, e_z= 0.12 which correspond to biaxialities l_σ = 0.2619 and l_ε = ±0.06, together with m=1, n=3. Here and in the rest of the paper we give all lengths s in units s_0 and energies e in units of e_0. The corresponding pair potential is shown in Fig.1. Notice that in this model the face to face potential well is rather shallow, so that competition from lateral ordering is relevant.

We have performed constant pressure simulations [20,21], where the sample box dimensions and thus the cell volume can change so as to adjust the system to its equilibrium density at the given thermodynamic state. This has in particular the advantage of avoiding the formation of holes in the sample. The well width parameter has been chosen as s_c =s_z. We have performed simulations at a series of temperatures in a cooling-down sequence of Monte Carlo runs started from well equilibrated configurations in the isotropic phase. We have employed a rectangular box with periodic boundary conditions, setting the dimensionless pressure P^* = $s_0{}^3 P/e_0$ =8 and allowing the box shape to change with a linear sampling of the volume V^*=$V/s_0{}^3$. Molecular orientations have been stored as quaternions. We have adopted a pair potential cut-off radius r_c = 4s_0, a Verlet neighbour list of radius r_l=5s_0, and the acceptance ratio for MC moves has been set to 0.4.

We have performed the computation of thermodynamic observables averaging over configurations sampled every 20 cycles, one cycle being a random sequence of N attempted MC moves. The simulation runs have not been shorter than 40 kcycles each for equilibration and production.

We have calculated a number of observables: thermodynamic quantities like density and enthalpy and orientational order parameters, in particular the uniaxial and the biaxial order parameters $<R^2_{00}>$ and $<R^2_{22}>$:

$$\langle R_{00}{}^2 \rangle = (3\langle \cos^2 \boldsymbol{b} \rangle - 1)/2 \qquad (4)$$

$$\langle R_{22}^2 \rangle = \left\langle \tfrac{1}{4} \left(1 + \cos^2 \beta \right) \cos 2\alpha \cos 2\gamma - \tfrac{1}{2} \cos \beta \sin 2\alpha \sin 2\gamma \right\rangle \qquad (5)$$

where $(\boldsymbol{a},\boldsymbol{b},\boldsymbol{g})$ is the set of Euler angles defining the orientation of a molecule in the director frame (see [19,22] for details of their computation). The latter orientational order parameter, which is different from zero only if the constituent particles are biaxial and the phase is biaxial is the most convenient one to employ as a monitor of phase biaxiality as discussed elsewhere [22].

RESULTS

We report in Fig. 2 our results for the temperature dependence of the density and the enthalpy of the two systems with opposite biaxialities. We see that at least a phase transition occurs at $T^* \sim 4.5$ for well depth biaxiality $\boldsymbol{l}_e = 0.06$ and at $T^* \sim 4.0$ for $\boldsymbol{l}_e = -0.06$. The change in density and enthalpy slopes (Fig.2) is more marked for $\boldsymbol{l}_e = -0.06$ which accordingly has a stronger first order character.
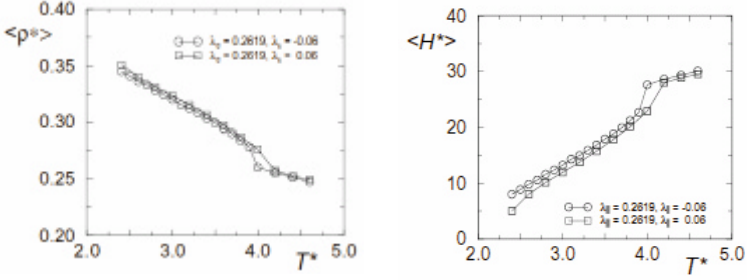
FIGURE 2 Density (left) and enthalpy (right) for the *NPT* simulation, $P^* =8$, of the two systems of biaxial GB particles, as indicated.

We also observe, from the $\langle R_{22}^2 \rangle$ vs. T* plot the onset of a biaxial phase for the system with $l_e = 0.06$, but not for the one with $l_e = -0.06$, at least in the fairly wide temperature range studied.
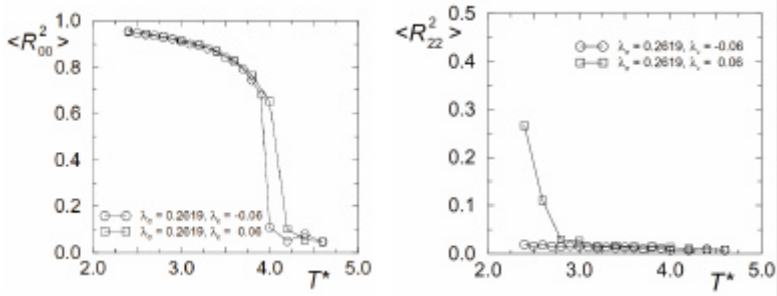

FIGURE 3 Orientational order parameters $\langle R^2_{00} \rangle$ and $\langle R^2_{22} \rangle$ for the two systems of $N = 1000$ GB discotic biaxial particles, as a function of   temperature. Dimensionless pressure is $P^* = 8$.

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We further characterize the biaxial phase by examining the radial distribution $g(r) = \langle d(r - r_{12}) \rangle_{12}/(4\boldsymbol{p}\, r^2 \boldsymbol{r})$ and the centre of mass density along the director $g(z) = \langle d(z - z_{12}) \rangle_{12}/(\boldsymbol{p}\, R^2 \boldsymbol{r})$ (R is the radius of a cylindrical sampling region and $z_{12} = \mathbf{r}_{12} \cdot \mathbf{n}$ is measured with respect to the director $\mathbf{n}$). In Fig.4 we show $g(r)$ and $g(z)$ at a selected temperature inside the biaxial phase. These show that the ordered phase is translationally uniform, and thus that the corresponding molecular organization is nematic. In particular we see that $g(z)$ does not have the characteristic long-range oscillations of a columnar phase [7,10], but just the relatively small wiggles corresponding to short range local packing.
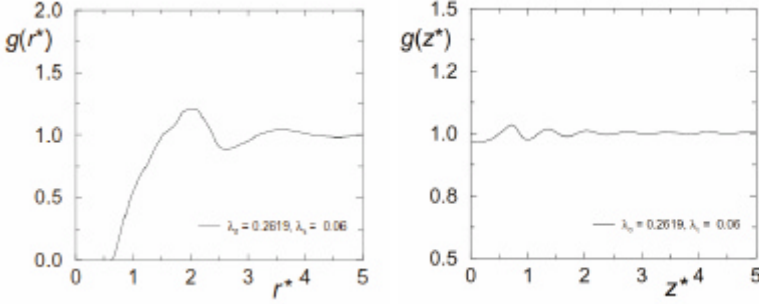

FIGURE 4   Radial correlation function $g(r)$ and density along the director $g(z)$ in the biaxial nematic phase of biaxial discotic GB particles ($\boldsymbol{l}_\sigma = 0.2619$ and $\boldsymbol{l}_\varepsilon = 0.06$) at T*=2.80.

It is instructive to examine snapshots of configurations of the phases formed by our two systems and in Figures 5,6 these are shown for two different views, one transversal and one parallel to the director. The molecules are represented with ellipsoids and their orientation is given by a colour code ranging from yellow to blue, providing an immediate visualization of the existing short-range and long-range order.
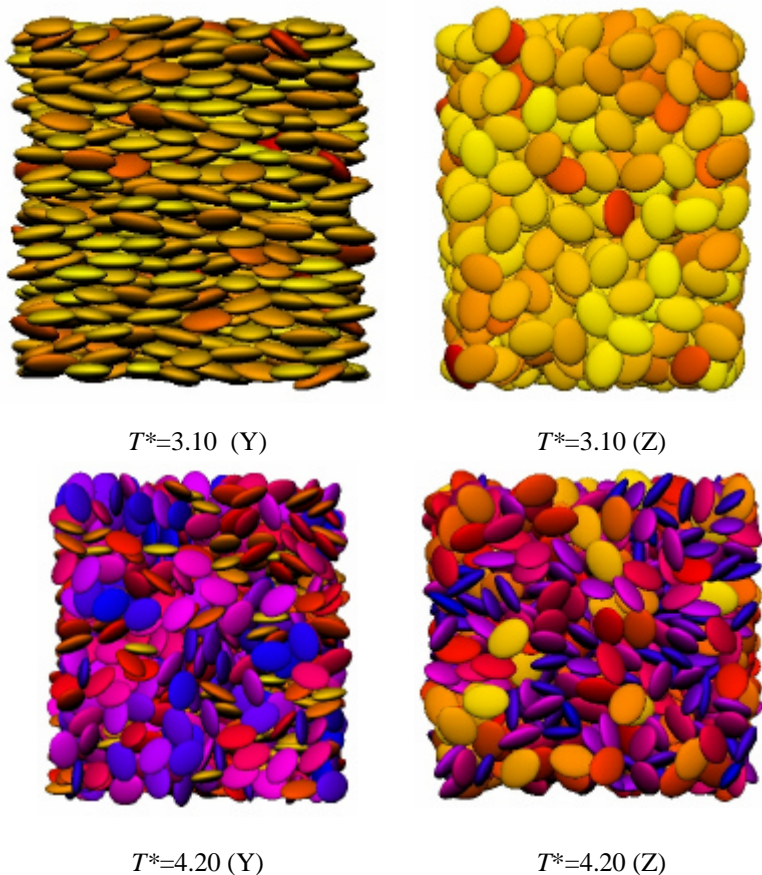
T*=3.10 (Y) T*=3.10 (Z)

T*=4.20 (Y) T*=4.20 (Z)

FIGURE 5 Top (Z) and transversal (Y) views of typical snapshots for the system of N = 1000 GB with I_{ε}= -0.06 at T*=3.10 (uniaxial nematic), 4.20 (isotropic), as obtained from *NPT* MC simulations, P* = 8. The colour code indicates the orientation of the molecular axis with respect to the director, ranging from parallel (yellow) to perpendicular (blue).

For the system of discs with biaxiality l_ε=-0.06 we have reported a configuration for a temperature in the nematic and one in the isotropic phase. It is apparent from the top view that the system is uniaxial and lacks columnar order. For the system with biaxiality l_ε= 0.06 we show snapshots from one temperature in the uniaxial (T*=3.60) and one in the biaxial (T*=2.40) phase. Here too we notice the lack of columnar structuring, but also that a change from uniaxial to biaxial ordering of the particles, fairly apparent from the top view of the sample, takes place.

The absence of a columnar phase is likely due to our choice of lateral interactions being stronger than facial ones. However, there is also a possibility that the system forms a glass before reaching the desired organization. Glassy phases have been reported in molecular dynamics simulations of rod-like GB particles [23], with a thousand fold decrease in diffusion constants. To check if the phases obtained here are still fluid or not, even though in our MC studies we do not have access to real dynamics, we have calculated the mean square displacements along the different directions α in the director frame, $\langle l_\alpha^* \rangle = \sqrt{\langle (\Delta r_\alpha^*)^2 \rangle}$, that we report in Fig.7. We see that the displacement is greater in the directions transversal to the director, being essentially the same in the two directions, so that no biaxiality is apparent here. The displacement along the director is slower but comparable to that of normal GB particles and although it obviously decreases with temperature, it does not show any evidence of a glass transition characterized by a sudden decrease of mobility.
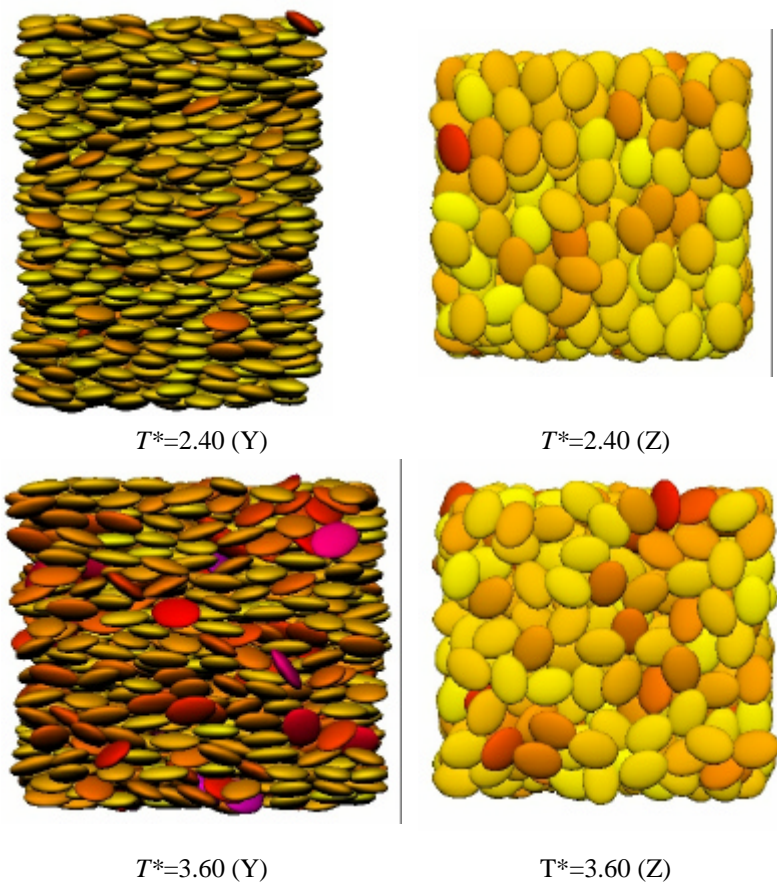
T*=2.40 (Y)   *T**=2.40 (Z)

T*=3.60 (Y)   T*=3.60 (Z)

FIGURE 6   Top (Z) and transversal (Y) views of typical snapshots of configurations for the system of biaxial GB discotic with l_e =0.06 in the biaxial (T* = 2.40) and uniaxial (T* = 3.60) phases.
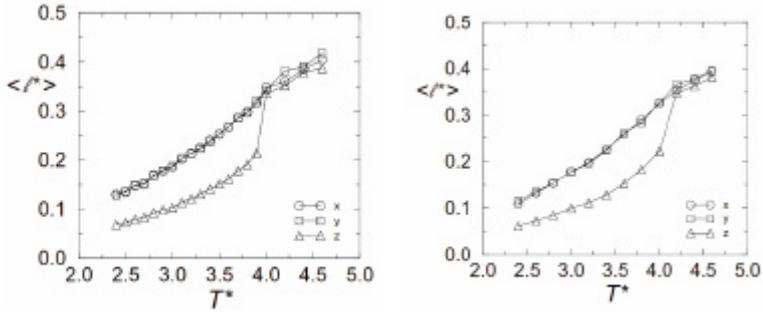
FIGURE 7 Mean square displacement $< \ell^* >$ as a function of temperature for the two systems of biaxial discotic particles: l_e =-0.06 (left) and l_e =0.06 (right).

In summary, we have observed the formation of biaxial nematic phases in systems of biaxial discotics Gay-Berne particles with a certain parameterization. Columnar phases were not observed for the two models studied here.

Acknowledgements

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