

now published as:

R. Berardi, S. Orlandi, C. Zannoni,

Columnar and interdigitated structures from apolar discotic mesogens with radial dipoles.  
A Monte Carlo study, *Liq. Cryst.*, 32, 1427-1436 (2005)

## Columnar and interdigitated structures from apolar discotic mesogens with radial dipoles. A Monte Carlo study

Roberto Berardi, Silvia Orlandi, and Claudio Zannoni

*Dipartimento di Chimica Fisica e Inorganica, and INSTM, Università,  
Viale del Risorgimento 4, 40136 Bologna, Italy*

### Abstract

We have simulated, using a Monte Carlo method, a system of apolar Gay–Berne discotic particles without dipoles and with two or three dipoles symmetrically embedded in the disc. The dipole-less system can form nematic and hexagonal columnar mesophases. Adding two in plane antiparallel radial dipoles has the effect of destabilising the columnar ordering, in favour of a fully interdigitated arrangement of the molecular stacks, with strong correlations in the plane perpendicular to the director and large biaxiality. No columnar phase is observed for the systems with three planar radial dipoles with threefold symmetry up to very low temperatures. Finally, decreasing the strength of the three dipoles, a columnar non-interdigitated phase is observed.

### Introduction

Discotics form an important and rapidly growing family of liquid crystals [1]. The typical structure of a discotic is that of a flat core with a certain number of chains attached [1, 2]. The central core has been realised with a large variety of aromatic structures, starting in particular from the classic triphenylene and truxene ones, to include now superyines, coronenes, phthalocyanines and a large variety of other moieties [3, 4, 5]. This flexibility in the choice of structures allows the possibility of selecting cores and inserting groups that confer to the molecule properties of interest in view of applications, such as charge transfer ability or a suitable charge distribution. One of the most promising application of columnar systems is in ‘molecular wires’, where regularity seems to be important to enhance electron or hole mobility along the column [6]. In order to understand at least some of the general aspects and

---

This paper is dedicated to Prof. G.R. Luckhurst in occasion of his 65th birthday.

trends involved, a molecular model, rather than an atomistic one requiring to address a specific compound, is of use.

One of the simplest possibilities to control ordering seems to be that of introducing substituents that endow the molecules with one or more dipole moments [7]. Understanding the effects on phase organisation of these dipole moments is on one hand not obvious, given the complex interplay between the different intermolecular contributions, and on the other essential from the point of view of a rational molecular design of new discotic materials [8].

Here we have modelled the discotic mesogen using a Gay–Berne (GB) [9, 10, 11] attractive–repulsive potential without dipoles and with a set of two and three embedded dipoles located at selected positions in the molecular plane, to examine their overall molecular and dipolar organisation. We have employed Monte Carlo (MC) ‘experiments’ to investigate several temperatures corresponding to nematic and columnar liquid crystal phases in the isobaric-isothermal (NPT) ensemble, paying attention to the characterisation of the low temperature phase, that is found to be particularly sensitive to the dipolar configuration.

## 1 Model

We have considered uniaxial oblate particles with axes  $\sigma_e$  and  $\sigma_s$  ( $\sigma_e < \sigma_s$ ) without dipoles, and with  $n = 2, 3$  embedded lateral planar electric point dipoles placed off centre [12], so as to give  $D_{nh}$  symmetry, as shown in figure 1, while positions and orientations of dipoles are given in table 1.

| Symmetry | Dipole | $\alpha$ | $\beta$ | $r_x$                 | $r_y$         | $r_z$ |
|----------|--------|----------|---------|-----------------------|---------------|-------|
| $D_{2h}$ | 1      | 0        | 90°     | $\sigma_s/4$          | 0             | 0     |
|          | 2      | 0        | 270°    | $-\sigma_s/4$         | 0             | 0     |
| $D_{3h}$ | 1      | 0        | 60°     | $\sqrt{3}/8\sigma_s$  | $\sigma_s/8$  | 0     |
|          | 2      | 0        | 180°    | 0                     | $-\sigma_s/4$ | 0     |
|          | 3      | 0        | 300°    | $-\sqrt{3}/8\sigma_s$ | $\sigma_s/8$  | 0     |

Table 1: *Position and orientation of dipoles in the  $D_{2h}$  and  $D_{3h}$  model discotic particles.*

The pair potential is the sum of a Gay–Berne and a dipole–dipole term:  $U_{ij}^* \equiv U_{ij}/\epsilon_s = U_{ij}^{GB*} + U_{ij}^{d*}$ . The Gay–Berne term has a repulsive and attractive contribution with a 12–6 inverse distance dependence form

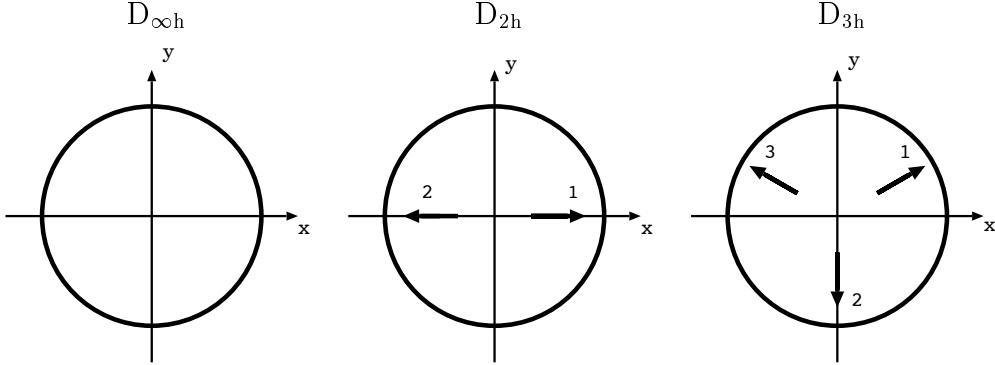


Figure 1: A sketch of the  $D_{nh}$  molecular model employed, showing position and orientation of the permanent dipoles.

$$\begin{aligned}
 U_{ij}^{GB*} &= 4\epsilon(\hat{\mathbf{z}}_i, \hat{\mathbf{z}}_j, \hat{\mathbf{r}}) \\
 &\times \left[ \left\{ \frac{\sigma_e}{r - \sigma(\hat{\mathbf{z}}_i, \hat{\mathbf{z}}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^{12} - \left\{ \frac{\sigma_e}{r - \sigma(\hat{\mathbf{z}}_i, \hat{\mathbf{z}}_j, \hat{\mathbf{r}}) + \sigma_e} \right\}^6 \right], \quad (1)
 \end{aligned}$$

with unit vectors  $\hat{\mathbf{z}}_i$ ,  $\hat{\mathbf{z}}_j$  defining the orientation of the principal axes of particles  $i$  and  $j$  taken along their symmetry axes, while  $\mathbf{r} = \mathbf{r}_j - \mathbf{r}_i \equiv r\hat{\mathbf{r}}$  is the intermolecular vector of length  $r$ .

Since here we are dealing with general trends, we employ the same parameterisation used in [12, 13] and based on the dimensions of a triphenylene core, namely: shape anisotropy  $\sigma_e/\sigma_s = 0.345$ , interaction anisotropy  $\epsilon_e/\epsilon_s = 5$ , and using GB parameters  $\mu = 1$  and  $\nu = 3$ . The coefficients  $\sigma_s$  and  $\epsilon_s$  are used as molecular units of length and energy. The cutoff radius adopted is  $r_c = 1.4\sigma_s$ . We have shown elsewhere that this discotic GB system, with a single axial [12] and transverse [13] dipole, yields a discotic nematic and hexagonal columnar phase. The pair dipolar energy term is given by

$$U_{ij}^{d*} = \frac{\mu_i^* \mu_j^*}{r^3} [\hat{\boldsymbol{\mu}}_i \cdot \hat{\boldsymbol{\mu}}_j - 3(\hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{r}})(\hat{\boldsymbol{\mu}}_j \cdot \hat{\mathbf{r}})]. \quad (2)$$

Here, we have used reduced dipole moments  $\mu^* = (\mu^2/\epsilon_s\sigma_s^3)^{1/2} = 0.6$  and  $\mu^* = 0.4$  which, when considering for instance a molecular diameter of  $\sigma_s \approx 10\text{\AA}$ , and an energy term  $\epsilon_s = 5 \times 10^{-15}\text{erg}$ , correspond to about 1.2D and 0.8D. The electrostatic energy has been evaluated using the reaction field method [14] with reaction field radius  $r_{RF} = 3\sigma_s$  and with a dielectric

continuum permittivity  $\epsilon_{RF} = 1.5$ . This was shown to be adequate in comparison with the more rigorous Ewald summation for this type of systems as shown in previous works [15, 16, 17].

Simulations were run in the isobaric–isothermal (NPT) ensemble (constant number of molecules  $N = 1000$ , dimensionless pressure  $P^* \equiv P\sigma_s^3/\epsilon_s = 5$  and dimensionless temperature  $T^* \equiv k_B T/\epsilon_s$ ), using periodic boundary conditions. All MC runs were started from well equilibrated isotropic configurations of the dipole–less system and a cubic box and were run in a cooling sequence with equilibration runs of  $\approx 300$  kcycles, where a cycle corresponds to  $N$  attempted MC moves. The box shape was adjusted during volume update moves in order to avoid the formation of holes. Box edges are allowed to vary in length independently, but are kept mutually orthogonal.

## 2 Results and discussion

We have determined from the simulations some useful physical quantities: average energies  $\langle U^{GB*} \rangle$ ,  $\langle U^{d*} \rangle$ , and orientational order parameters [18], i.e.

$$\langle R_{00}^2 \rangle = \langle P_2 \rangle = \langle (3 \cos^2 \beta - 1)/2 \rangle, \quad (3)$$

and

$$\langle R_{22}^2 \rangle = \langle (1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma/4 - \cos \beta \sin 2\alpha \sin 2\gamma/2 \rangle, \quad (4)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are the Euler angles giving the orientation of the molecular axis system ( $\hat{\mathbf{x}}$ ,  $\hat{\mathbf{y}}$ ,  $\hat{\mathbf{z}}$ ) in the director frame ( $\hat{\mathbf{X}}$ ,  $\hat{\mathbf{Y}}$ ,  $\hat{\mathbf{Z}}$ ).

Phase structure has been characterised through the radial distribution function

$$g_0(r) = 1/(4\pi r^2 \rho) \langle \delta(r - r_{ij}) \rangle_{ij}, \quad (5)$$

and its second rank anisotropy

$$g_2^+(r) = \langle \delta(r - r_{ij}) P_2(\cos \beta_{ij}) \rangle_{ij}, \quad (6)$$

where  $\beta_{ij}$  is the angle between the intermolecular vector  $\mathbf{r}_{ij}$  and the phase director  $\hat{\mathbf{Z}}$ [10], and the average  $\langle \dots \rangle_{ij}$  is computed over all molecular pairs.

We now briefly comment on each of the various systems studied.

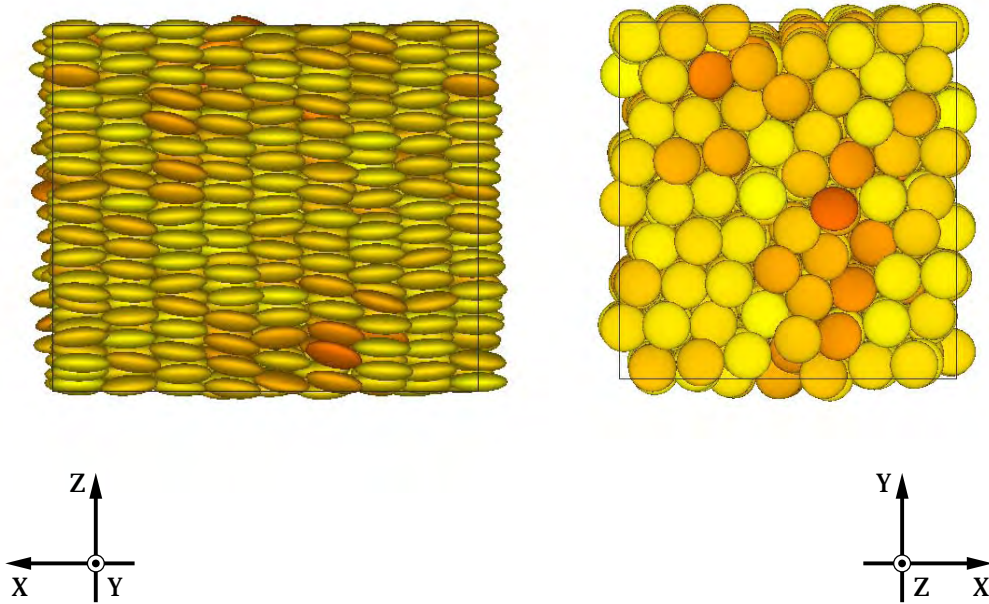


Figure 2: *Snapshots of MC-NPT configurations (side and top views) of systems of  $N = 1000$  dipole-less GB discs at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase  $C_h$ ). The orientation of the director frame is also shown.*

## 2.1 Dipole-less ( $D_{\infty h}$ )

Starting from the highest temperature studied  $T^* = 8.0$ , the first observation is that the system is isotropic. As temperature is reduced, orientational order develops and molecules organise in a nematic and then, by further lowering  $T^*$ , in a columnar hexagonal phase. Snapshots of the molecular organisations, at  $T^*$  corresponding to the columnar phase, are shown in figure 2, where we have colour coded the orientations of the molecules relative to the phase director, in order to highlight their orientational ordering.

We plot in figure 3 the temperature dependence of the average energy per particle, and uniaxial and biaxial order parameters for the systems studied, while numerical values of the observables and phase assignments are reported in the table given in the Appendix. The order parameter  $\langle R_{00}^2 \rangle$  increases sharply when the nematic is formed, at  $T^* = 6.4$ , and grows regularly with no significant jumps when the columnar phase is formed. The biaxial  $\langle R_{22}^2 \rangle$  parameter is zero within error at all temperatures and it is shown as a check.

The  $g_0(r)$  (figure 2a), presents, for the low temperature columnar phase ( $T^* = 4.0$ ), several well defined peaks related to the detailed structure of this mesophase. In particular, the first two maxima at  $r^* = 0.35, 0.7$  cor-

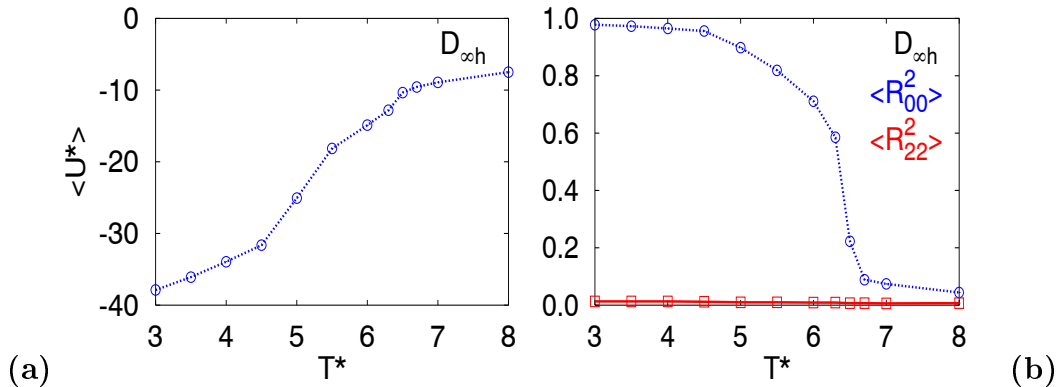


Figure 3: Average total energy per particle  $\langle U_{ij}^* \rangle$  (a), and orientational and biaxial order parameters  $\langle R_{00}^2 \rangle$  and  $\langle R_{22}^2 \rangle$  (b) for a system of  $N = 1000$  dipole-less GB discs at  $P^* = 100$  as a function of temperature  $T^*$ .

respond to the first two neighbouring pairs within the same column. The next two maxima are due to adjacent pairs of molecule belonging to different columns and their position indicates an hexagonal arrangement of interdigitated columns. An increase in temperature ( $T^* = 6.0$ ) gives a nematic phase and the radial correlation function shows no positional ordering: side-by-side configurations are approximately as probable as face-to-face.

Further details on the phase structure can be obtained studying the second rank anisotropy  $g_2^+(r)$  (figure 4b). In correspondence of the columnar phases the anisotropy exhibits a detailed structure even for high molecular separations showing two positive maxima for the intra-column neighbouring pairs (intermolecular vector parallel to the director) and a third negative peak corresponding to molecules belonging to adjacent columns (intermolecular vector perpendicular to the director).

## 2.2 Two dipoles ( $D_{2h}$ )

The introduction of two antiparallel dipoles has quite a pronounced effect on the phase behaviour. Examining the order (see figure 5b) first, we see that the transition from the isotropic to a uniaxially ordered system ( $\langle R_{00}^2 \rangle \neq 0$ ,  $\langle R_{22}^2 \rangle = 0$ ) is still taking place roughly in the same temperature region ( $T^* \approx 6$ ) as for the dipole-less system. Moreover at  $T^* \approx 5$  a new, strongly biaxial, molecular organisation sets in. Correspondingly to the biaxial ordering  $\langle R_{22}^2 \rangle > 0$  the energy shows a significant stabilisation due to the electrostatic energy (see figure 5a). It is immediately clear that the structure is quite different from the standard columnar organisation by a comparison of the radial distributions  $g_0(r)$  and  $g_2^+(r)$  shown in figure 6. We notice that

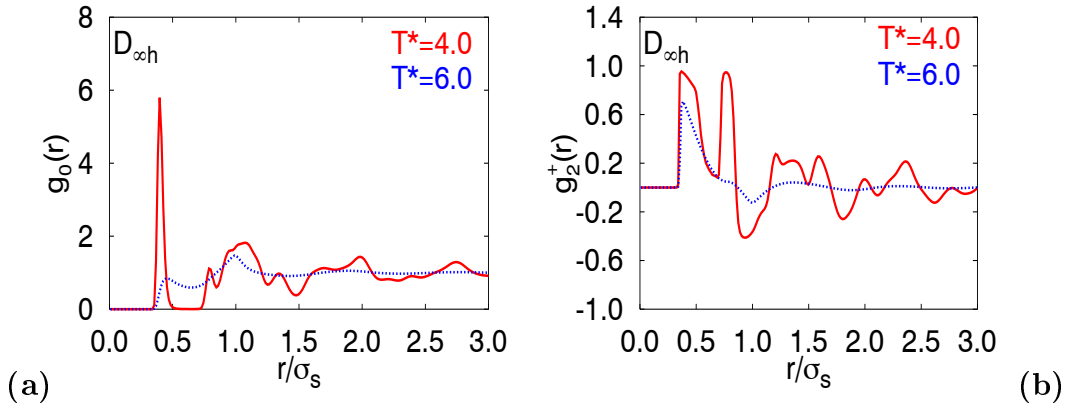


Figure 4: *Radial correlation function  $g_0(r)$  (a), and second rank anisotropy  $g_2(r)$  (b), for systems of  $N = 1000$  dipole-less GB discs at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase  $C_h$ ) and 6.0 (phase  $N$ ).*

even if the structure seems more disordered, some positional ordering of the phase still exists as shown by the  $g_0(r)$  peaks.

The nature of the phase organisation becomes clear when observing typical snapshots from the simulation in the biaxial region (figure 7) that indicate a regular intercalated structure with local pairing of dipoles from neighbouring molecules. This effective dipole locking explains the electrostatic energy contribution increase (figure 5a). The observed interdigitation is highly directional in the direction perpendicular to the director. We notice that although the two antiparallel dipoles imply a non vanishing molecular quadrupole, the effect of their off-centre position, which allows interlocking, is quite different from that expected from a central quadrupole, as studied in [20, 21].

### 2.3 Three dipoles ( $D_{3h}$ )

We now turn to the last case studied, where a third dipole is added to the discotic core as in figure 1, re-establishing an effective cylindrical symmetry since, at least from the point of view of second rank order parameters a  $D_{3h}$  axis has the same effect of a  $D_{\infty h}$  one. An immediate consequence is that  $\langle R_{22}^2 \rangle = 0$  and no biaxial phase is present (see figures 8b and 11b). It might be expected that the normal columnar phase is also re-established, but this is not necessarily so. In fact, the organisation obtained depends on the strength of the dipoles moment as we have shown considering two cases:  $\mu^* = 0.4$  and  $\mu^* = 0.6$ . Indeed, for  $\mu^* = 0.6$  the intermolecular dipole-dipole interaction leads to the disappearance of the columnar phase and a highly ordered uniaxial nematic phase has been observed down to very low

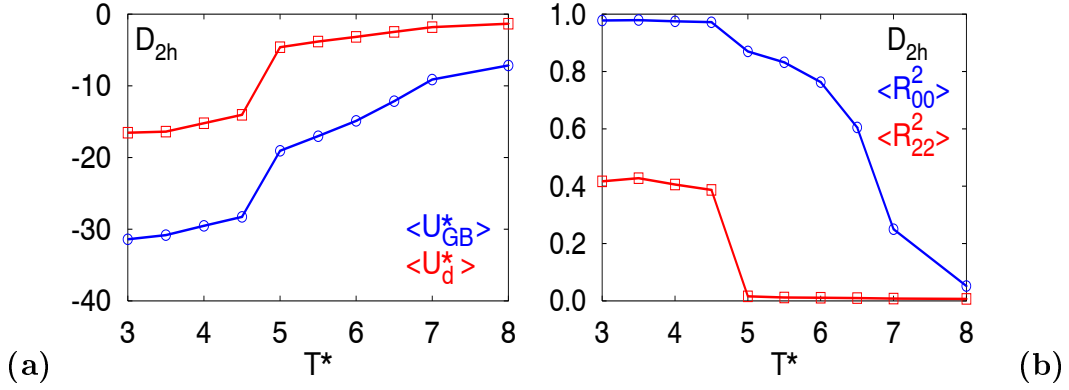


Figure 5: Average GB and dipolar energy contributions  $\langle U_{ij}^{GB*} \rangle$  and  $\langle U_{ij}^{d*} \rangle$  (a), and orientational and biaxial order parameters  $\langle R_{00}^2 \rangle$  and  $\langle R_{22}^2 \rangle$  (b) for a system of  $N = 1000$  GB discs with two planar dipoles at  $P^* = 100$  as a function of temperature  $T^*$ .

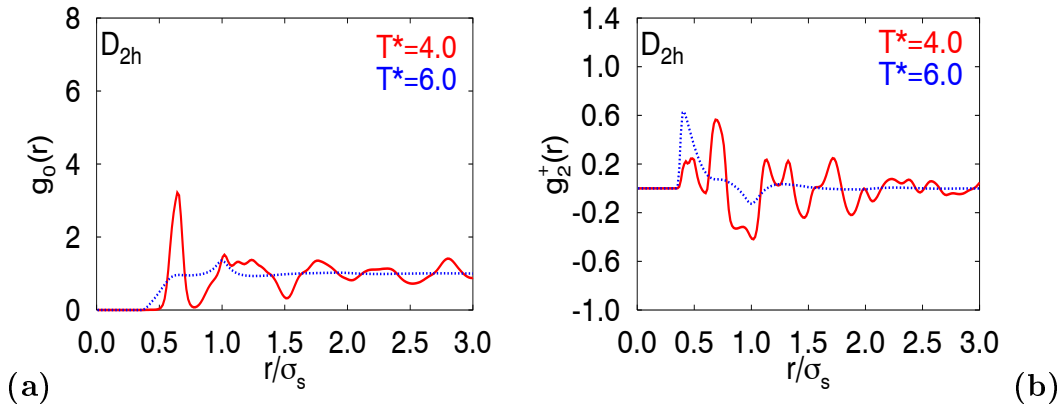


Figure 6: Radial correlation function  $g_0(r)$  (a), second rank anisotropy  $g_2(r)$  (b), for systems of  $N = 1000$  GB discs with two planar dipoles at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase  $N_{bx}$ ), and 6.0 (phase  $N$ ).



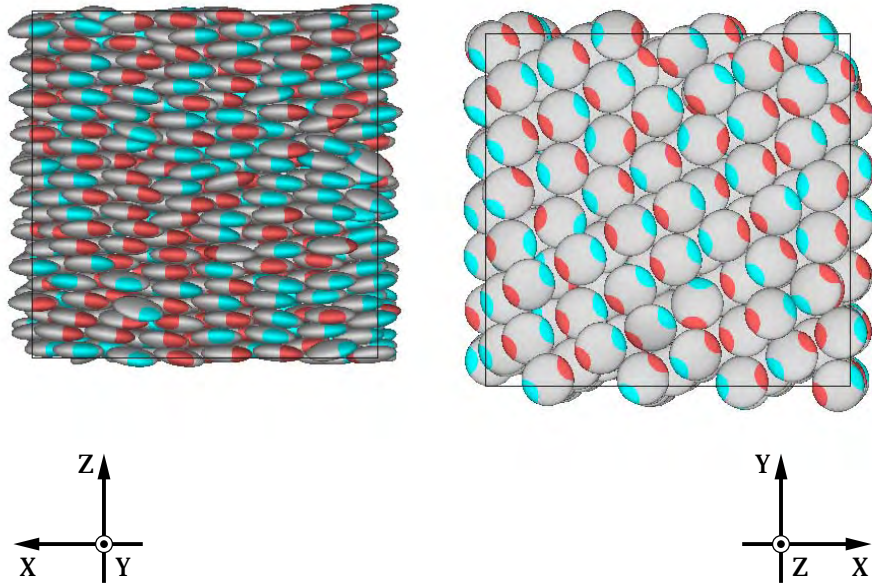


Figure 7: *Snapshots of MC-NPT configurations (side and top views) of systems of  $N = 1000$  GB discs with two planar dipoles at  $P^* = 100$  and temperature  $T^* = 4.0$  (phase  $N_{bx}$ ). The red and cyan ‘patches’ label the molecular dipoles, and the director frame is also shown.*

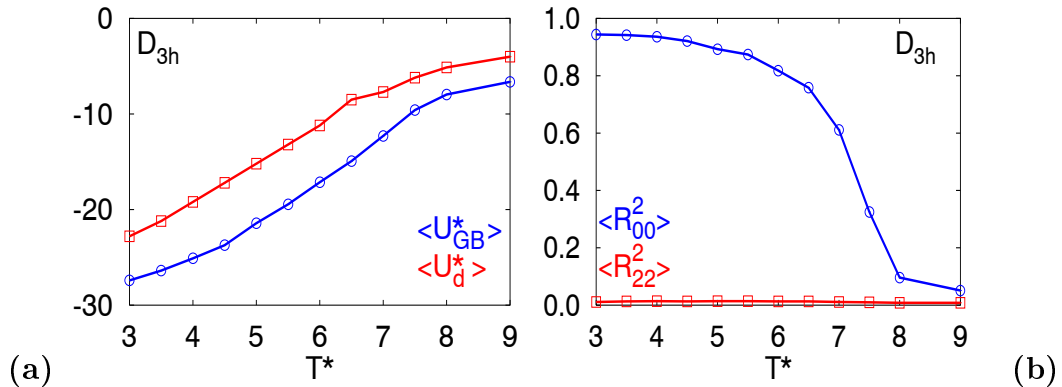


Figure 8: Average GB and dipolar energy contributions  $\langle U_{ij}^{GB*} \rangle$  and  $\langle U_{ij}^{d*} \rangle$  (a), and orientational and biaxial order parameters  $\langle R_{00}^2 \rangle$  and  $\langle R_{22}^2 \rangle$  (b) for a system of  $N = 1000$  GB discs with three planar dipoles  $\mu^* = 0.6$  at  $P^* = 100$  as a function of temperature  $T^*$ .

temperatures. On the other hand, for the weaker dipole  $\mu^* = 0.4$ , molecules are stacked in columns like for the previous dipole-less case and a short range order of the dipoles along the columns axis is observed (see figures 10 and 13).

To characterise the order in columnar stacks we calculate the angular distribution of  $\theta_{i,j}$ , the angle between the  $\hat{\mathbf{x}}$  axis of a given molecule  $i$ , and the  $\hat{\mathbf{x}}$  axis of a molecule  $j$  in the same column. We consider first ( $j = i + 1$ ) and second ( $j = i + 2$ ) neighbours, as well as molecules separated by distance equal to half stack. Notice that for the  $D_{3h}$ ,  $\mu^* = 0.4$  system the  $\hat{\mathbf{x}}$  axis is geometrically correlated to the direction of the three dipoles, while for the dipole-less  $D_{\infty h}$  system, the  $\hat{\mathbf{x}}$  is an arbitrary fixed axis. An examination of figure 14 confirms that for the dipole-less system no preferred orientation about the axes of the columns in which they are stacked exists, and that all orientations  $\theta_{i,j}$  are equivalent. Instead, in the  $D_{3h}$  case, dipolar interactions introduce an orientational correlation along the column axis; however, this angular correlation is short-ranged, and no long range transversal angular correlation lasting across the column has been found.

### 3 Conclusions

Our Monte Carlo simulations of Gay-Berne discs with local symmetrically placed dipoles have shown that the introduction of the dipolar interaction can have a profound influence on the phase organisation, even for molecules that are overall apolar.

All the systems studied show a transition from isotropic to nematic and

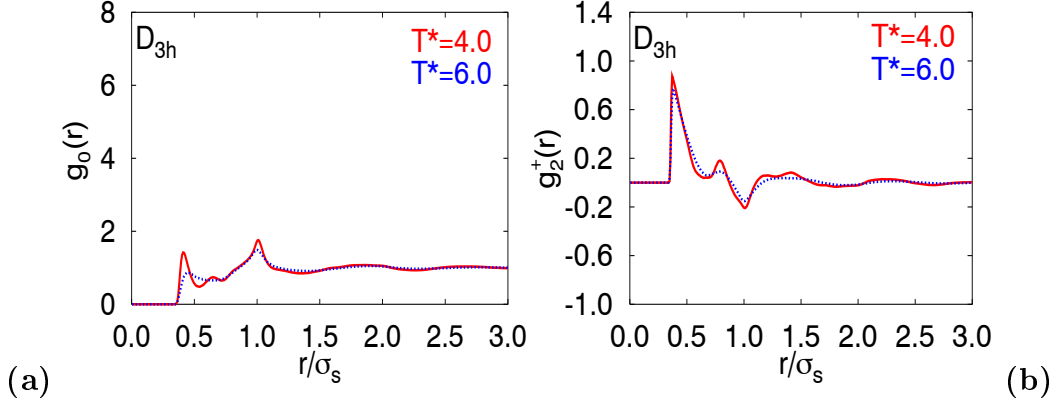


Figure 9: Radial correlation function  $g_0(r)$  (a), second rank anisotropy  $g_2(r)$  (b) for systems of  $N = 1000$  GB discs with three planar dipoles at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase N) and  $6.0$  (phase N).

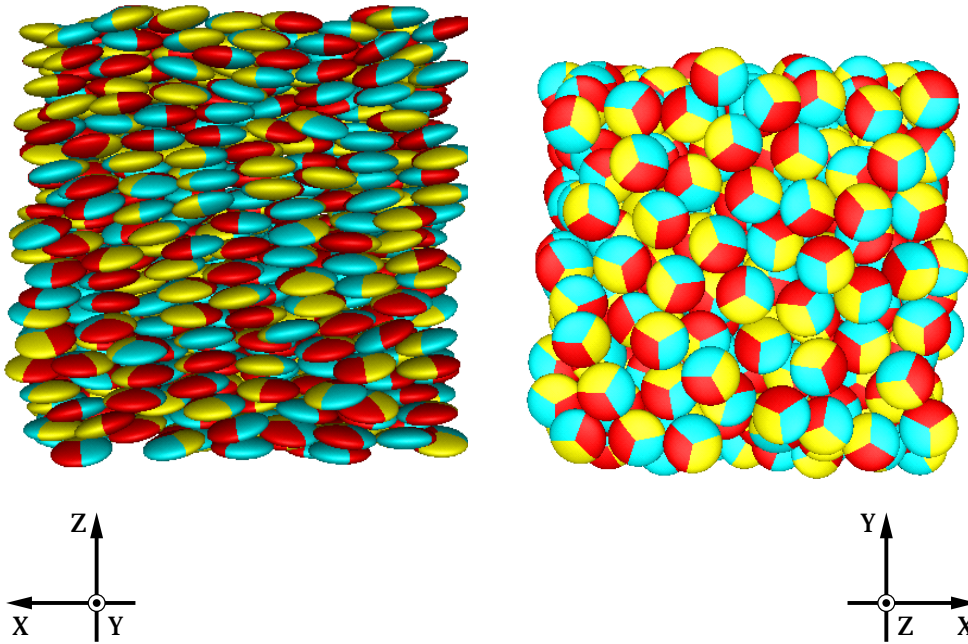


Figure 10: Snapshots of MC-NPT configurations (side and top views) of systems of  $N = 1000$  GB discs with three dipoles  $\mu^* = 0.6$  at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase N).

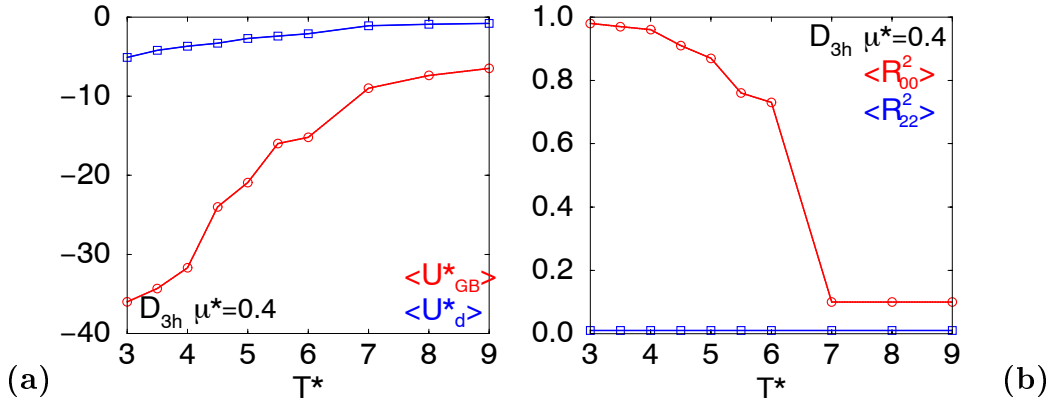


Figure 11: Average GB and dipolar energy contributions  $\langle U_{ij}^{GB*} \rangle$  and  $\langle U_{ij}^{d*} \rangle$  (a), and orientational and biaxial order parameters  $\langle R_{00}^2 \rangle$  and  $\langle R_{22}^2 \rangle$  (b) for a system of  $N = 1000$  GB discs with three planar dipoles  $\mu^* = 0.4$  at  $P^* = 100$  as a function of temperature  $T^*$ .

from nematic to a high ordered phase which is strictly dependent on dipoles configuration and strength. Dipole-less Gay-Berne discotic particles form isotropic, nematic and hexagonal columnar mesophases, with weak correlations between columns. The columnar phase is destabilised by the addition of two or three strong lateral planar dipoles. For two and three planar dipoles  $\mu^* = 0.6$ , in fact, no columnar structure is observed down to  $T^* = 3.0$ , finding instead a strongly ordered nematic phase, while when dipoles are absent or with strength decreased, low temperature organisations correspond to columnar phases. We notice that for the discs with two or three symmetrical dipoles the electrostatic energy is always negative with a magnitude which, for the dipole strength  $\mu^* = 0.6$  is at most 40% of the GB energy. The antiparallel association of the lateral dipoles gives rise to interdigitation between the different columns with the creation of less packed structures. In the two dipoles case, at low temperature, discotics are strongly interdigitated and show strong correlations in the plane perpendicular to the director and a large biaxiality.

No columnar phase is shown for the system with three relatively strong planar dipoles up to very low temperatures. Molecular stacks are completely interdigitated and no long-range in-column transversal order is observed. However, changes of dipole strength have a significant effect on intra and inter columnar arrangement. In particular decreasing the strength of the three planar dipoles we again observe a columnar non interdigitated phase, as in the apolar system.

We did not find evidence of chain structures, as found in many dipolar

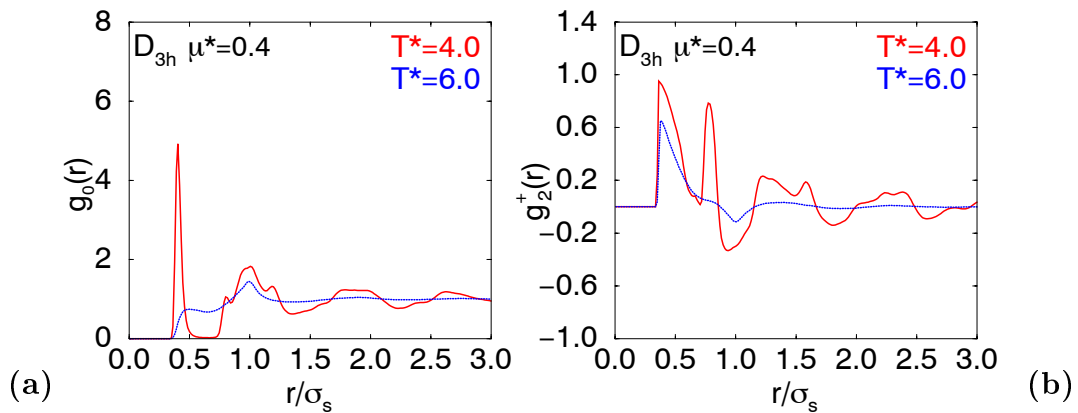


Figure 12: *Radial correlation function  $g_0(r)$  (a), second rank anisotropy  $g_2(r)$  (b) for systems of  $N = 1000$  GB discs with three planar dipoles  $\mu^* = 0.4$  at  $P^* = 100$  and temperatures  $T^* = 4.0$  (phase  $C_h$ ) and  $6.0$  (phase  $N$ ).*

systems [22] because of the favourable head–tail disposition of point dipoles, but this is not surprising since our particles are non–polar overall and their dipoles are placed symmetrically and far apart (see figure 1), differently, e.g. from rod–like particles with transverse dipole [17, 22].

## Acknowledgements

We wish to thank University of Bologna, MIUR (PRIN Cristalli Liquidi), EU project NAIMO (IP 500355), and INSTM for financial support.

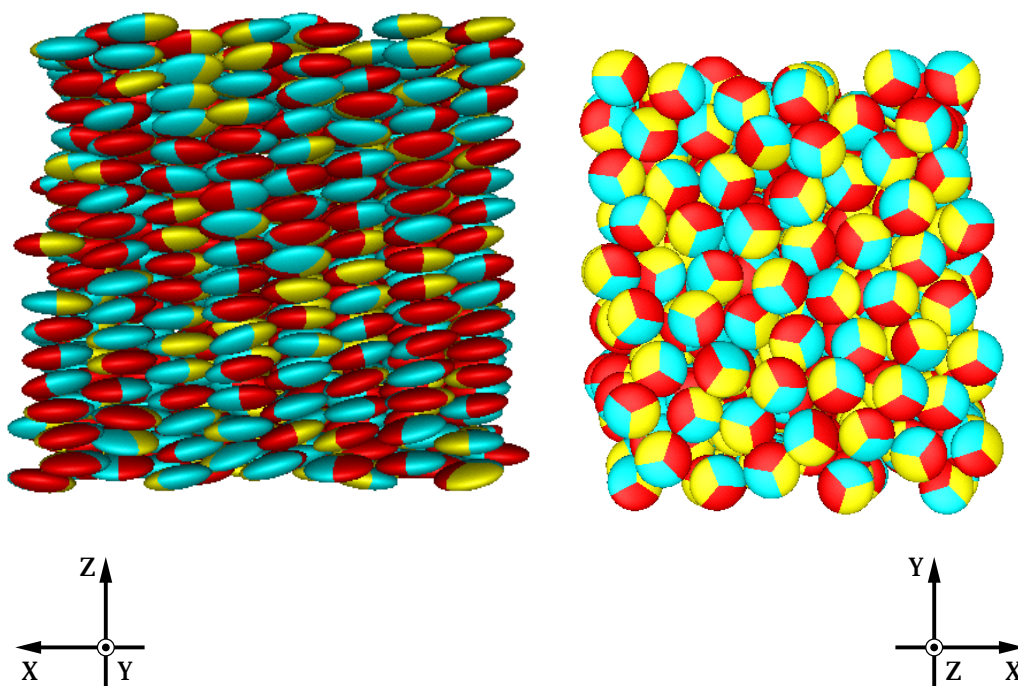


Figure 13: *Snapshots of MC-NPT configurations (side and top views) of systems of  $N = 1000$  GB discs with three dipoles  $\mu^* = 0.4$  at  $P^* = 100$  and temperature  $T^* = 4.0$  (phase  $C_h$ ).*

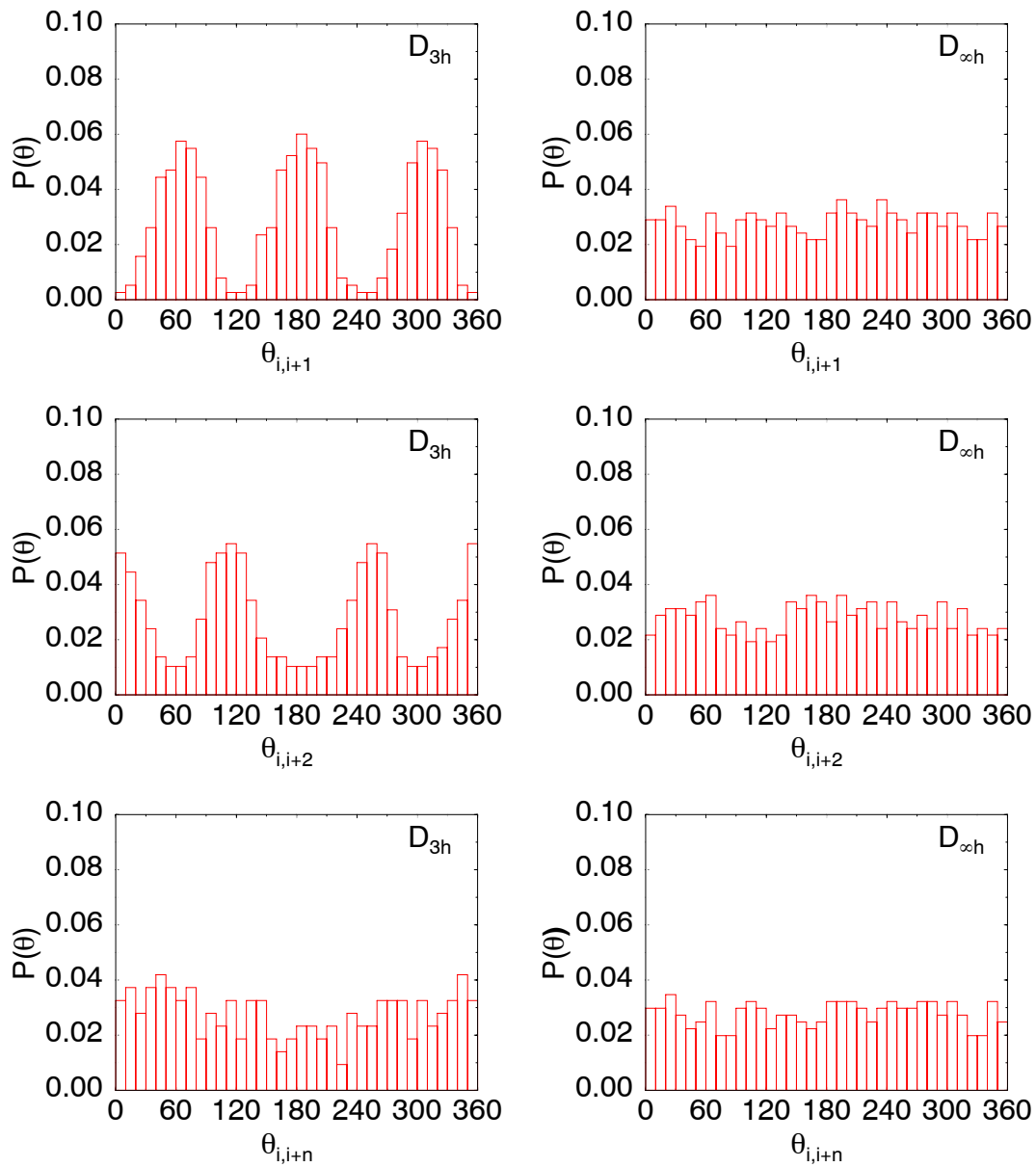


Figure 14: Distribution of angular twist  $\theta_{i,j}$  along the columns for system with three dipoles  $\mu^* = 0.4$  (left column,  $D_{3h}$ ) and  $\mu^* = 0.0$  (right column,  $D_{\infty h}$ ) at  $T^* = 4.0$ . The three cases correspond to first ( $\theta_{i,i+1}$ ) and second ( $\theta_{i,i+2}$ ) neighbours, and to half column separation ( $\theta_{i,i+n}$ ).

# Appendix

|                                       | $T^*$                                 | phase          | $\langle U_{ij}^{GB*} \rangle$ | $\langle U_{ij}^{d*} \rangle$ | $\langle R_{00}^2 \rangle$ | $\langle R_{22}^2 \rangle$ |
|---------------------------------------|---------------------------------------|----------------|--------------------------------|-------------------------------|----------------------------|----------------------------|
| <b>no dipoles</b>                     | 3.0                                   | $C_h$          | $-37.9 \pm 0.2$                | -                             | $0.98 \pm 0.01$            | -                          |
|                                       | 3.5                                   | $C_h$          | $-36.0 \pm 0.2$                | -                             | $0.97 \pm 0.01$            | -                          |
|                                       | 4.0                                   | $C_h$          | $-33.9 \pm 0.2$                | -                             | $0.97 \pm 0.01$            | -                          |
|                                       | 4.5                                   | $C_h$          | $-31.6 \pm 0.2$                | -                             | $0.96 \pm 0.01$            | -                          |
|                                       | 5.0                                   | $N$            | $-25.1 \pm 0.2$                | -                             | $0.90 \pm 0.01$            | -                          |
|                                       | 5.5                                   | $N$            | $-18.1 \pm 0.2$                | -                             | $0.82 \pm 0.01$            | -                          |
|                                       | 6.0                                   | $N$            | $-14.9 \pm 0.2$                | -                             | $0.71 \pm 0.01$            | -                          |
|                                       | 6.25                                  | $N$            | $-12.8 \pm 0.2$                | -                             | $0.59 \pm 0.01$            | -                          |
|                                       | 6.5                                   | $I$            | $-10.3 \pm 0.2$                | -                             | $0.22 \pm 0.01$            | -                          |
|                                       | 6.75                                  | $I$            | $-9.6 \pm 0.2$                 | -                             | $0.1 \pm 0.01$             | -                          |
|                                       | 7.0                                   | $I$            | $-8.9 \pm 0.2$                 | -                             | $0.1 \pm 0.01$             | -                          |
| 8.0                                   | $I$                                   | $-7.5 \pm 0.2$ | -                              | $0.1 \pm 0.01$                | -                          |                            |
| <b>two dipoles</b>                    | 3.0                                   | $N_{bx}$       | $-31.4 \pm 0.2$                | $-16.6 \pm 0.2$               | $0.98 \pm 0.01$            | $0.42 \pm 0.01$            |
|                                       | 3.5                                   | $N_{bx}$       | $-30.8 \pm 0.2$                | $-16.4 \pm 0.2$               | $0.98 \pm 0.01$            | $0.42 \pm 0.01$            |
|                                       | 4.0                                   | $N_{bx}$       | $-29.5 \pm 0.2$                | $-15.2 \pm 0.2$               | $0.98 \pm 0.01$            | $0.40 \pm 0.01$            |
|                                       | 4.5                                   | $N_{bx}$       | $-28.3 \pm 0.2$                | $-14.0 \pm 0.2$               | $0.97 \pm 0.01$            | $0.38 \pm 0.01$            |
|                                       | 5.0                                   | $N$            | $-19.1 \pm 0.2$                | $-4.6 \pm 0.2$                | $0.87 \pm 0.01$            | -                          |
|                                       | 5.5                                   | $N$            | $-17.0 \pm 0.2$                | $-3.8 \pm 0.2$                | $0.83 \pm 0.01$            | -                          |
|                                       | 6.0                                   | $N$            | $-14.9 \pm 0.2$                | $-3.2 \pm 0.2$                | $0.76 \pm 0.01$            | -                          |
|                                       | 6.5                                   | $I$            | $-12.1 \pm 0.2$                | $-2.5 \pm 0.2$                | $0.60 \pm 0.01$            | -                          |
|                                       | 7.0                                   | $I$            | $-9.1 \pm 0.2$                 | $-1.8 \pm 0.2$                | $0.25 \pm 0.01$            | -                          |
|                                       | 8.0                                   | $I$            | $-7.2 \pm 0.2$                 | $-1.3 \pm 0.2$                | $0.1 \pm 0.01$             | -                          |
|                                       | <b>three dipoles</b><br>$\mu^* = 0.6$ | 3.0            | $N$                            | $-27.4 \pm 0.2$               | $-22.8 \pm 0.01$           | $0.94 \pm 0.01$            |
| 3.5                                   |                                       | $N$            | $-26.4 \pm 0.2$                | $-21.2 \pm 0.2$               | $0.94 \pm 0.01$            | -                          |
| 4.0                                   |                                       | $N$            | $-25.1 \pm 0.2$                | $-19.2 \pm 0.2$               | $0.94 \pm 0.01$            | -                          |
| 4.5                                   |                                       | $N$            | $-23.7 \pm 0.2$                | $-17.2 \pm 0.2$               | $0.92 \pm 0.01$            | -                          |
| 5.0                                   |                                       | $N$            | $-21.4 \pm 0.2$                | $-15.2 \pm 0.2$               | $0.88 \pm 0.01$            | -                          |
| 5.5                                   |                                       | $N$            | $-19.5 \pm 0.2$                | $-13.1 \pm 0.2$               | $0.87 \pm 0.01$            | -                          |
| 6.0                                   |                                       | $N$            | $-17.1 \pm 0.2$                | $-11.2 \pm 0.2$               | $0.82 \pm 0.01$            | -                          |
| 6.5                                   |                                       | $I$            | $-14.9 \pm 0.2$                | $-8.5 \pm 0.2$                | $0.76 \pm 0.01$            | -                          |
| 7.0                                   |                                       | $I$            | $-12.3 \pm 0.2$                | $-7.7 \pm 0.2$                | $0.61 \pm 0.01$            | -                          |
| 7.5                                   |                                       | $I$            | $-9.6 \pm 0.2$                 | $-6.2 \pm 0.2$                | $0.32 \pm 0.01$            | -                          |
| 8.0                                   |                                       | $I$            | $-8.0 \pm 0.2$                 | $-5.1 \pm 0.2$                | $0.1 \pm 0.01$             | -                          |
| 9.0                                   | $I$                                   | $-6.6 \pm 0.2$ | $-4.0 \pm 0.2$                 | $0.1 \pm 0.01$                | -                          |                            |
| <b>three dipoles</b><br>$\mu^* = 0.4$ | 3.0                                   | $C_h$          | $-36.8 \pm 0.2$                | $-4.8 \pm 0.1$                | $0.98 \pm 0.01$            | -                          |
|                                       | 3.5                                   | $C_h$          | $-34.8 \pm 0.2$                | $-4.3 \pm 0.1$                | $0.97 \pm 0.01$            | -                          |
|                                       | 4.0                                   | $C_h$          | $-32.4 \pm 0.2$                | $-3.8 \pm 0.1$                | $0.96 \pm 0.01$            | -                          |
|                                       | 4.5                                   | $N$            | $-22.0 \pm 0.2$                | $-3.2 \pm 0.1$                | $0.89 \pm 0.01$            | -                          |
|                                       | 5.0                                   | $N$            | $-20.4 \pm 0.2$                | $-2.9 \pm 0.1$                | $0.87 \pm 0.01$            | -                          |
|                                       | 5.5                                   | $N$            | $-18.0 \pm 0.2$                | $-2.4 \pm 0.1$                | $0.84 \pm 0.01$            | -                          |
|                                       | 6.0                                   | $N$            | $-15.2 \pm 0.2$                | $-1.9 \pm 0.1$                | $0.74 \pm 0.01$            | -                          |
|                                       | 7.0                                   | $I$            | $-9.1 \pm 0.2$                 | $-1.2 \pm 0.1$                | $0.10 \pm 0.01$            | -                          |
|                                       | 8.0                                   | $I$            | $-7.5 \pm 0.2$                 | $-0.9 \pm 0.1$                | $0.07 \pm 0.01$            | -                          |
|                                       | 8.0                                   | $I$            | $-6.5 \pm 0.2$                 | $-0.7 \pm 0.1$                | $0.07 \pm 0.01$            | -                          |

Table: Results from MC-NPT simulations at pressure  $P^* = 100$  of a system of  $N = 1000$  GB discotic molecules for the Gay-Berne and dipolar energies per particle  $\langle U_{ij}^{GB*} \rangle$  and  $\langle U_{ij}^{d*} \rangle$ , the orientational order parameter  $\langle R_{00}^2 \rangle$  and the biaxial order parameter  $\langle R_{22}^2 \rangle$  at temperatures  $T^*$  corresponding to isotropic (I), nematic (N) and columnar ( $C_h$ ) phases as indicated.



## References

- [1] Guillon, D., 1999, *Structure and Bonding*, **95**, 41.
- [2] Chandrasekhar, S., 1992, *Liquid Crystals*, 2nd ed. (Cambridge: Cambridge U.P.).
- [3] Kumar, S., 2004, *Liq. Cryst.*, **31**, 1037.
- [4] Praefcke, K. and Holbrey, J. D., 1996, *J. of Inclusion Phenom. Mol. Recognition Chem.*, **24**, 19.
- [5] Ringsdorf, H., Wüstefeld, R., Zerta, E., Ebert, M., and Wendorff, J. H., 1989, *Angew. Chem. Int. Ed.*, **28**, 914.
- [6] Cornil, J., Lemaire, V., Calbert, J. P., and Brédas, J. L., 2002, *Adv. Mat.*, **14**, 726.
- [7] Attias, A-J., Cavalli, C., Donnio, B., Guillon, D., Hapiot, P., and Malthête, J., 2004, *Mol. Cryst. Liq. Cryst.*, **415**, 169.
- [8] Roussel, O., Kestemont, G., Tant, J., de Halleux, V., Gómez Aspe, R., Levin, J., Remacle, A., Raluca Gearba, I., Ivanov, D., Lehmann, M., Geerts, Y., 2003, *Mol. Cryst. Liq. Cryst.*, **396**, 35.
- [9] Zannoni, C., 2001, *J. Mat. Chem.*, **11**, 2637, and refs. therein.
- [10] Berardi, R., Emerson, A. P. J. and Zannoni, C., 1993, *J. Chem. Soc. Faraday Trans.*, **89**, 4069.
- [11] Emerson, A. P. J., Luckhurst, G. R., Whatling, S. G., 1994, *Mol. Phys.*, **82**, 113.
- [12] Berardi, R., Orlandi, S. and Zannoni, C., 1997, *J. Chem. Soc. Faraday Trans.*, **93**, 1493.
- [13] Berardi, R., Orlandi, S., and Zannoni, C., 2000, *PCCP*, **2**, 2933.
- [14] Barker, J. A. and Watts, R. O., 1973, *Mol. Phys.*, **26**, 789.
- [15] Gil-Vilegas, A., McGrother, S. and Jackson, G., 1997, *Mol. Phys.*, **92**, 723.
- [16] Houssa, M., Oualid, A. and Rull, L. F., 1998, *Mol. Phys.*, **94**, 439. .

- [17] Berardi, R., Orlandi, S. and Zannoni, C., 1999, *Int. J. Mod. Phys. C*, **10**, 477.
- [18] Biscarini, F., Chiccoli, C., Pasini, P., Semeria, F., and Zannoni, C., 1995, *Phys. Rev. Lett.*, **75**, 1803.
- [19] Jaster, A., 1999, *Phys. Rev. E*, **59**, 2594.
- [20] Bates, M. A., Luckhurst, G. R., 1998, *Liq. Cryst.*, **24**, 229.
- [21] Neal, M. P., Parker, A. J., 2001, *Phys. Rev. E*, **63**, 011706.
- [22] Gil-Villegas, A., McGrother, S. C., and Jackson, G., 1997, *Chem. Phys. Lett.*, **269**, 441.