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Phase diagram of hard board-like colloids from computer simulations†

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The rich mesophase polymorphism and the phase sequence of board-like colloids depends critically on their shape anisometry. Implementing extensive Monte Carlo simulations, we calculated the full phase diagram of sterically interacting board-like particles, for a range of experimentally accessible molecular dimensions/anisometries of colloids of this shape. A variety of self organized mesophases including uniaxial and biaxial nematics, smectic, cubatic and columnar phases have been identified. Our results demonstrate clearly that the molecular anisometry influences critically not only the structure and the symmetry of the mesophases but also, and perhaps more interestingly, the phase sequence between them. New classes of phase sequences such as nematic–nematic and, for the first time, a direct transition from a discotic and a biaxial nematic to an orthogonal smectic A phase have been identified. The molecular geometry requirements for such phase behavior have been located.

Colloidal suspensions of sterically interacting anisometric particles exhibit a rich variety of mesophases and phase transformations between them.[1,2] The local structure and eventually the macroscopic behavior of these self-organized anisotropic fluids are entropy driven since they are determined mainly by excluded volume interactions.[1,3,4] Recently, colloidal dispersions of board-like goethite particles were demonstrated[2] to exhibit, in addition to the usual uniaxial nematic phases, a spontaneously formed stable biaxial nematic phase as well as a series of nematic–nematic (N–N) phase transitions under the influence of external fields.[5] At high concentrations these systems exhibit smectic and/or columnar phases with structures that have not yet been unambiguously identified.

The possibility of formation of stable biaxial nematic phases by D_{2h}-symmetric hard board-like particles with a so called "dual shape", *i.e.* particles having almost equal length to width and width to thickness ratios, was predicted theoretically four decades ago by Straley.[6] Surprisingly, since then there have been no computer simulation studies of this particularly simple model with the exception of the simulations by Bates *et al.*[7] In these simulations, however, the orientation of the long axis of the particles were completely aligned, thus preventing the possibility of an orientationally isotropic fluid. On the other hand it has been shown that hard biaxial ellipsoids of certain anisometries exhibit stable uniaxial and biaxial nematic phases.[8] However, as it has been pointed out by Bolhuis and Frenkel,[9] this system is unlikely to exhibit positionally ordered liquid crystalline (LC) phases and indeed it does not.[8] This is an inherent weakness of the hard ellipsoid model, preventing the study of the relative stability of the nematic state with respect to the positionally ordered LC states, which are always present in the phase sequence of real board-like colloidal suspensions.[2]

To overcome the weaknesses of the aforementioned models, we model the board-like particles as hard spheroplatelets (SPs), a tractable model introduced by Mulder[10] for analytical calculations as a generalization of the well studied spherocylinder model. A SP particle consists of a rectangular box with dimensions $(l - d) \times (w - d) \times d$, capped at its corners by quarter spheres of diameter d and half cylinders on its sides with diameter d and length $(l - d)$ or $(w - d)$ forming a convex body of orthorhombic symmetry (see Fig. 1). Without loss of generality we assume that $l \geq w \geq d$ and assign a body fixed frame as shown in Fig. 1. The dimensionless length and width are given by $l^* = l/d$ and $w^* = w/d$ respectively. When $w^* = 1$ the SP particle becomes a spherocylinder with aspect ratio $l^* - 1$; a system whose phase diagram is well known for a wide range of aspect ratios from the seminal works of Bolhuis and Frenkel[9] and McGrother *et al.*[11] At the $w^* = l^*$ limit the SP particle transforms into a tetragonal spheroplatelet (D_{4h} symmetry) and becomes very similar to the tetragonal parallelepiped particles simulated by John *et al.*[12]

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† Electronic supplementary information (ESI) available: Phase diagram of hard spheroplatelets with pairs (w^*,l^*) in which simulations have been performed (S1); representative equations of state (S2); cubatic phase (S3). See DOI: 10.1039/c3sm51165k

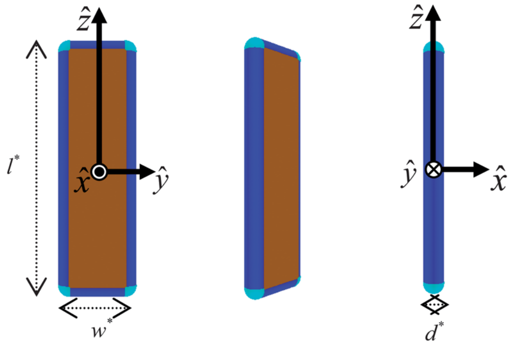

Fig. 1 Views of the simulated hard board spheroplatelet particles.

The phase behavior and the molecular organization of the SPs is studied here by Metropolis Monte Carlo computer simulations in the isothermal isobaric ensemble (*NpT*) using variable size simulation boxes with periodic boundary conditions.[13] Most of the simulations were performed for $N \approx 1000$ particles although much larger systems were simulated in certain cases. The pressure (p^*) *versus* packing fraction (η) equation of state (EOS) of each simulated system in the (l^*,w^*) space, was calculated with compression runs from the isotropic phase. Here $\eta = Nv/\bar{V}$ is the packing fraction, v is the molecular volume, $p^* = pv/k_BT$ is the reduced pressure and $\bar{V}$ is the ensemble average of the volume of the simulated system at p^* (representative EOS are given in ESI S2†). Expansion series from highly packed ordered phases were performed as well to check whether the observed phase sequence on compression includes metastable (over-compressed) states. Since our prime interest in this communication is the LC behavior of the SP systems, we present results for particles with sizes in the range of $5 \leq l^* < 12$ and $1 < w^* < 12$. SPs with $l^* < 5$ freeze directly into crystalline phases or into long lived glassy states. Systems with $l^* = 5$ and $w^* < 2$ exhibit, in accordance with previous studies, a rather narrow range of stable smectic A (SmA) ordering before they crystallize;[9,11] mesomorphism is removed from the phase sequence when $w^* > 2$.

To trace the phase transition boundaries between the isotropic and the nematic phase we have identified the orientational symmetry of the phases and the associated order parameters through diagonalization of the order tensors,[8] $\boldsymbol{Q}^{\boldsymbol{a}} = \sum_{i=1}^{N}(3(\boldsymbol{a}_i \cdot \boldsymbol{A})(\boldsymbol{a}_i \cdot \boldsymbol{B}) - \delta_{\boldsymbol{AB}})/2N$, where $\boldsymbol{a} = (\hat{\boldsymbol{x}},\hat{\boldsymbol{y}},\hat{\boldsymbol{z}})$ is any of the molecular symmetry axes and $\boldsymbol{A}$,$\boldsymbol{B}$ denote the axes $\hat{\boldsymbol{X}}$,$\hat{\boldsymbol{Y}}$,$\hat{\boldsymbol{Z}}$ of the simulation box. The onset of positionally ordered phases is usually accompanied by clear density jumps in the p^*–η EOS. Visual inspection and combined analysis of the orientational/positional order through the calculation of appropriate projections of the radial pair correlation functions,[14] allows the location of the phase transition pressures and an unambiguous classification of the positionally ordered states.

The mesophases of different ordering exhibited by the simulated systems in the range $5 \leq l^* < 12$ are: (i) two uniaxial nematic phases, a calamitic (N_+) and a discotic (N_-) phase, with the *z*- and the *x*-molecular axes aligned along the unique director respectively, (ii) two biaxial nematic phases (N_{b+} and N_{b-}) with the common alignment of the *z*- and *x*-molecular axes defining the primary director in N_{b+} and in N_{b-} respectively, (iii) uniaxial SmA phases with the long *z*-molecular axis oriented along the layer normal, (iv) columnar phases (Col_X) either uniaxial or biaxial with the *x*-molecular axis oriented along the columns in all cases and (v) cubatic (Cub) mesophases.

Starting from the low pressure (packing fraction) isotropic state (I) and compressing the systems up to their crystallization or vitrification pressures we calculated the complete phase diagram in the w^*–l^* parameter space. It is presented in Fig. 2, where the differently colored domains correspond to the following enantiotropic phase sequences: I–[N_+]–SmA, I–[N_{b-}–N_{b+}]–SmA, I–N_-–SmA, I–[N_-]–Col_X and I–Cub; the brackets here indicate phases that may be absent from the phase transition sequence, *i.e.* the notation I–[N_+]–SmA means that direct I–SmA as well as I–N_+–SmA phase sequences are possible, as indicated by the green and light blue colored regions in Fig. 2. Clearly the phase diagram of Fig. 2 is symmetric with respect to the $l^* = w^*$ line. The solid line (Straley's line) represents molecular geometries with $l^* = w^{*2}$ for which, according to theoretical considerations,[6,10] the particles are of "dual shape" – neither prolate nor oblate – and biaxially ordered phases are expected.

The phase diagram of Fig. 2 reveals that the $(l_c^*,w_c^*) \approx (9,3)$ point corresponds to a critical molecular anisometry. At this point the system exhibits a direct I–SmA phase transition on compression. However, even a small deviation from this specific molecular anisotropy, leads to severe changes in the phase sequence/stability. To facilitate the discussion on the phase behavior of particles with dimensions close to the critical geometry we present in Fig. 3 three distinct topologies of the p^*–w^* phase diagram corresponding to SPs having a reduced

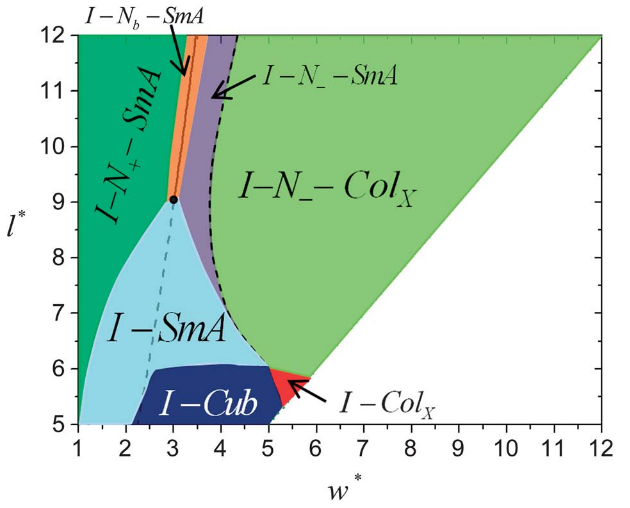

Fig. 2 The phase diagram of hard spheroplatelets as a function of their molecular geometry parameters. Different colored regions correspond to different phase sequences. The boundaries between the regions are estimates inferred from the analysis of a large number of MC simulations at several SP molecular geometries (l^*,w^*), (see ESI S1†). Straley's line is also plotted (black solid line). The black circle corresponds to the critical molecular geometry $(l_c^*,w_c^*) = (9,3)$.

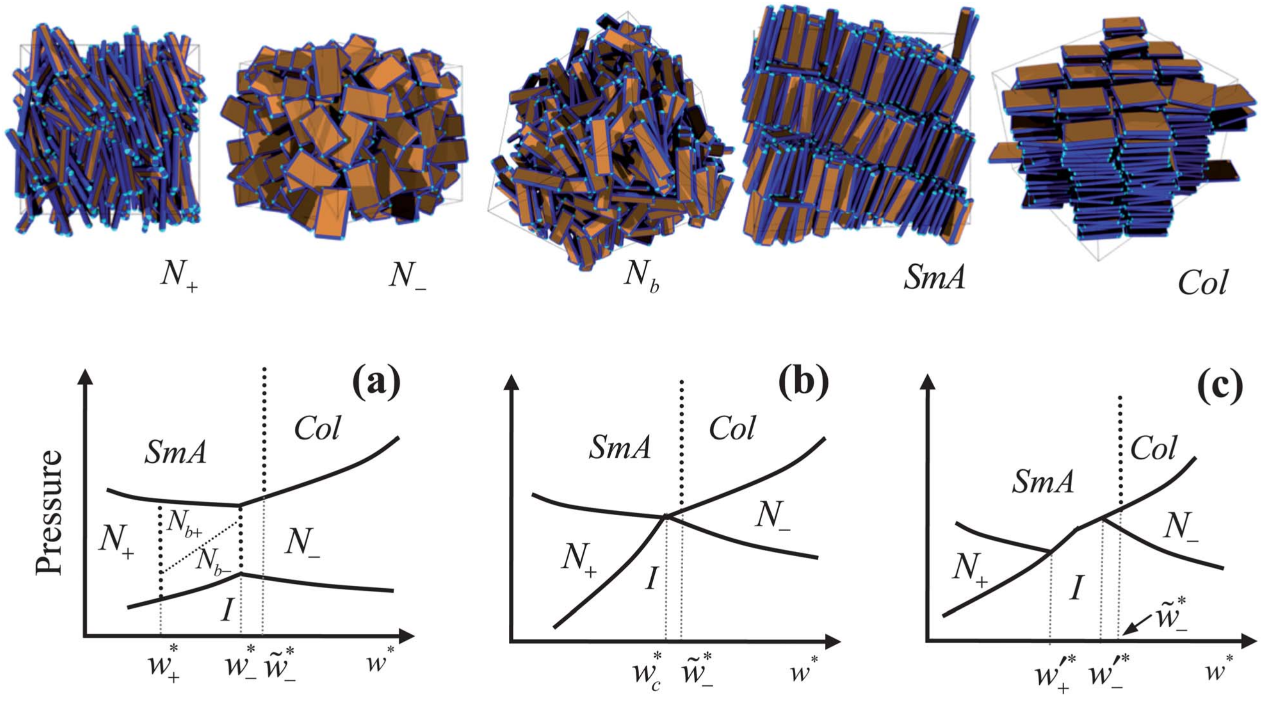

Fig. 3 Pressure *vs.* molecular width qualitative phase diagram topologies for the molecular lengths: (a) $l^* > l_c^*$, (b) $l^* = l_c^*$, and (c) $l^* < l_c^*$. Representative snapshots of the liquid crystalline phases are also shown.

length l^* slightly above (Fig. 3a), equal (Fig. 3b) and slightly below (Fig. 3c) of the critical length l_c^*.

For lengths $l^* > l_c^*$ the first ordered phases observed upon compression are different types of nematics. The symmetry and structure of the nematic phase depends on the width w^*, see Fig. 3a. Specifically, for $w^* < w_+^*$ a calamitic nematic (N_+) is obtained, while for $w^* > w_-^*$ the phase is discotic (N_-). In both cases the N–I phase transition has a weakly first order character. Here, $w_{(+/-)}^*$ are the l^*-dependent critical SP widths that determine the limits of stability of the uniaxial nematic phases. For SPs with widths in the narrow window $w_+^* < w^* < w_-^*$ a stable biaxial nematic phase enters into the phase sequence. The values of $w_{(+/-)}^*$ are difficult to determine precisely from the simulations due to the almost second order nature of the N–I phase transition in this window. To exclude the possibility that the biaxial nematic phases are artifacts due to the size of the simulated systems, much larger systems ($N \approx 4000$) were simulated and they confirmed our findings. The long range nature of the biaxial order of the N_b phases was confirmed with the calculation of a series of rotationally invariant pair correlation functions.[14]

Perhaps the most striking finding in this range of molecular geometries is the crossover, N_{b-}–N_{b+}, between two distinct biaxial nematic states (in Fig. 3a the crossover pressures are indicated by the thin dotted line that divides the biaxial window). These low and high pressure (packing fraction) biaxial nematics, although of the same macroscopic symmetry, differ in the molecular axis that determines the principal director of the phase. This packing fraction driven change of the main director of the nematic phase is expected to have profound implications on the alignment and/or the response of these phases upon the application of external aligning fields. Such a N–N phase transition is supported by the Landau–de Gennes theory for biaxial nematics,[15] and was predicted for systems of biaxial particles with the help of Onsager type molecular theory by Taylor and Herzfeld[16] and more recently confirmed by Martínez-Ratón *et al.*[17] with a more elaborate density functional theory that goes beyond the second-order virial approximation.

All the nematic phases in the $l^* > l_c^*$ region transform upon compression through a first order phase transition, into either SmA or Col mesophases. The observation, however, that not only the N_+ phase but the biaxial and, for a narrow range of reduced molecular widths $w_-^* < w^* < \tilde{w}_-^*$, the N_- phase as well, transform into uniaxial (rod-like) SmA phases reveals a new class of phase transitions which, to the best of our knowledge, have not been reported previously for thermotropic or colloidal mesophases. Here, $\tilde{w}_-^*$ denotes the molecular width that determines the boundary between the N_-–SmA and the N_-–Col phase sequences.

The biaxial nematic states are not present in systems with molecular lengths $l^* < l_c^*$ (see Fig. 2 and 3c). For these molecular elongations, the two uniaxial nematic phases are gradually reduced into the ranges $w^* < w'^*_+$ and $w^* > w'^*_-$ for the rod- and disc-like nematic phases respectively. In the intermediate range $w'^*_+ < w^* < w'^*_-$ nematicity is totally suppressed and a direct first order phase transition from the isotropic to a uniaxial SmA phase is observed. $l^* \approx 6$ corresponds to the lower molecular length below which the nematic state disappears completely from the phase sequence. For $l^* < 6$ the systems condense from the isotropic phase directly into (i) the SmA phase for $w^* < 2.5$ or (ii) cubatic mesophases for $w^* > 2.5$ or (iii) the columnar phase for molecular widths $w^* \approx l^*$. The Cub phases, consist of well defined, short in length and highly ordered stacks of particles forming mesophases without a long range nematic-like orientational order. The cubatic-like ordering always appears through a strong first order phase transition either compressing the isotropic phase or expanding highly ordered, close packed states, usually with appreciable hysteresis (see ESI S3†). We note here, that the thermodynamic stability of the cubatic mesophases of the $l^* < 6$ systems is still under investigation. For a detailed discussion on the stability of the cubatic mesophase see ref. 18–20.

For $l^* < l_c^*$ the N_- phase appears in the phase sequence for $w^* > w'^*_-$ and, as in the case with $l^* > l_c^*$, for a narrow range of molecular widths ($w'^*_- < w^* < \tilde{w}^*_-$) it transforms upon compression into the SmA phase. The I–N_-–Col phase sequence is observed when $w^* > \tilde{w}^*_-$, (the $\tilde{w}^*_-$ boundary is indicated by the dashed line in Fig. 2). In the region $w'^*_- < w^* < \tilde{w}^*_-$ the N_- phase is thermodynamically stable for a small range of pressures (packing fractions). For these pressures the extent of SmA or Col ordering fluctuations in the simulated N_- phases are comparable with the size of the simulation box and this makes the precise determination of the $\tilde{w}^*_-$ -boundary difficult. For molecular geometries close to the $\tilde{w}^*_-$ line the competition between SmA and Col ordering, in combination with the unavoidable molecular size polydispersity in real systems is expected to enhance the stability of the nematic state in favor of the positionally ordered states.[7,21]

Our results suggest that at $l_c^* \approx 9$ (see Fig. 3b) the lines $w^*_{+/-}$ and $w'^*_{+/-}$ converge onto the critical point (l_c^*,w_c^*) at which the biaxial nematic phase, the two uniaxial nematics and the SmA phase meet. Interestingly the critical point (l_c^*,w_c^*) lies on Straley's line and defines, in terms of the molecular dimensions, the lower limit of stability of the biaxial nematic phase. In other words, according to our findings, Straley's condition $l^* = w^{*2}$ for biaxial nematics is valid provided that $l^* > 9$.

In conclusion, by performing and analyzing a large number of MC computational experiments we were able to trace the phase boundaries of sterically interacting SPs, a prototype that mimics the very basic features of real biaxial board-like colloids. Despite its simplicity, the model reproduces remarkably well many experimental observations on colloidal suspensions of board-like particles. We have identified new types of phase transformations that include (i) a N_{b-}–N_{b+} crossover and (ii) the direct transition from a discotic nematic or a biaxial nematic to a conventional orthogonal SmA mesophase. Our results provide a robust framework and a well defined reference system for understanding and interpreting the presence of more complex interactions in real colloids upon detecting deviations from the hard core model. These nearly exact computational experiments on the phase behavior of hard biaxial particles offer a comprehensive guide to experiments towards the design of colloidal systems with a desired functionality, as well as enhancing the theory for testing and improving analytical molecular models using simple intermolecular potentials.

Acknowledgements

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Notes and references

1 H. N. W. Lekkerkerker and G. J. Vroege, Liquid crystal phase transitions in suspensions of mineral colloids: new life from old roots, *Philos. Trans. R. Soc. London, Ser. A*, 2013, **371**, 20120263.

2 E. van den Pol, A. V. Petukov, D. M. E. Thies-Weesie, D. V. Byelov and G. J. Vroege, Experimental realization of biaxial liquid crystal phases in colloidal dispersions of boardlike particles, *Phys. Rev. Lett.*, 2009, **103**, 258301.

3 U. Agarwal and F. A. Escobedo, Mesophase behaviour of polyhedral particles, *Nat. Mater.*, 2011, **10**, 230–235.

4 P. F. Damasceno, M. Engel and S. C. Glotzer, Predictive Self-Assembly of Polyhedra into Complex Structures, *Science*, 2012, **337**, 453–457.

5 E. van den Pol, A. Lupascu, M. A. Diaconeasa, A. V. Petukov, D. V. Byelov and G. J. Vroege, Onsager revisited: magnetic field induced nematic–nematic phase separation in dispersions of goethite nanorods, *J. Phys. Chem. Lett.*, 2010, **1**, 2174–2178.

6 J. P. Straley, Ordered phases of a liquid of biaxial particles, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1974, **10**, 1881–1887.

7 A. G. Vanakaras, M. A. Bates and D. J. Photinos, Theory and simulation of biaxial nematic and orthogonal smectic phases formed by mixtures of board-like molecules, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3700–3706.

8 P. J. Camp and M. P. Allen, Phase diagram of the hard biaxial ellipsoid fluid, *J. Chem. Phys.*, 1997, **106**, 6681–6688.

9 P. Bolhuis and D. Frenkel, Tracing the phase boundaries of hard spherocylinders, *J. Chem. Phys.*, 1997, **106**, 666–687.

10 B. Mulder, Isotropic-symmetry-breaking bifurcations in a class of liquid-crystal model, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1989, **39**, 360–370.

11 S. C. McGrother, D. C. Williamson and G. Jackson, A re-examination of the phase diagram of hard spherocylinders, *J. Chem. Phys.*, 1996, **104**, 6755–6771.

12 B. S. John, C. Juhlin and F. A. Escobedo, Phase behavior of colloidal hard perfect tetragonal parallelepipeds, *J. Chem. Phys.*, 2008, **128**, 044909.

13 M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, New York, 2002.

14 R. Berardi and C. Zannoni, Do thermotropic biaxial nematics exist? A Monte Carlo study of biaxial Gay-Berne particles, *J. Chem. Phys.*, 2000, **113**, 5971–5979.

15 D. Allender and L. Longa, Landau–de Gennes theory of biaxial nematics reexamined, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2008, **78**, 011704.

16 M. P. Taylor and J. Herzfeld, Nematic and smectic order in a fluid of biaxial hard particles, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1991, **44**, 3742–3751.

17 Y. Martínez-Ratón, S. Varga and E. Velasco, Biaxial nematic phases in fluids of hard board-like particles, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13247–13254.

18 P. D. Duncan, A. J. Masters and M. R. Wilson, Thermodynamic stability of the cubatic phase of hard cut spheres evaluated by expanded ensemble simulations, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 011702.

19 M. R. Wilson, P. D. Duncan, M. Dennison and A. J. Masters, Molecular dynamics simulation studies of platelets with square cross-sectional area: formation of a stable cubatic phase, *Soft Matter*, 2012, **8**, 3348–3356.

20 M. Marechal, A. Patti, M. Dennison and M. Dijkstra, Frustration of the Isotropic-Columnar Phase Transition of Colloidal Hard Platelets by a Transient Cubatic Phase, *Phys. Rev. Lett.*, 2012, **108**, 206101.

21 S. Belli, A. Patti, M. Dijkstra and R. van Roij, Polydispersity stabilizes biaxial nematic liquid crystals, *Phys. Rev. Lett.*, 2011, **107**, 148303.

S. D. Peroukidis and A. G. Vanakaras, Soft Matter, 2013, 9, 7419-7423.

Phase diagram of hard board like colloids from computer simulations

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Supplementary Information FILE

S1. Phase diagram of hard spheroplatelets with pairs $\left(w^*, l^*\right)$ in which simulations have been performed

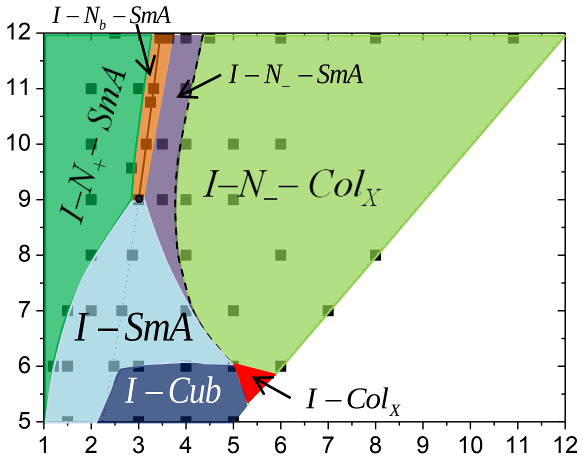

Fig. S1. The phase diagram of hard spheroplatelets (see main manuscript for details). The black squares on the diagram indicate the molecular geometries $\left(w^*, l^*\right)$ for which the actual simulations were performed.

S2. Representative Equations of State (EOS)

We present characteristic pressure (p^*) versus packing fraction (η) equations of state for various $\left(w^*, l^*\right)$ pairs. More specifically, for the following enantiotropic phase sequences: (a) $I-N_--Col_X$, (b) $I-N_--SmA$ (c) $I-SmA$, and (d) $I-N_b-SmA$(see Fig. S2).

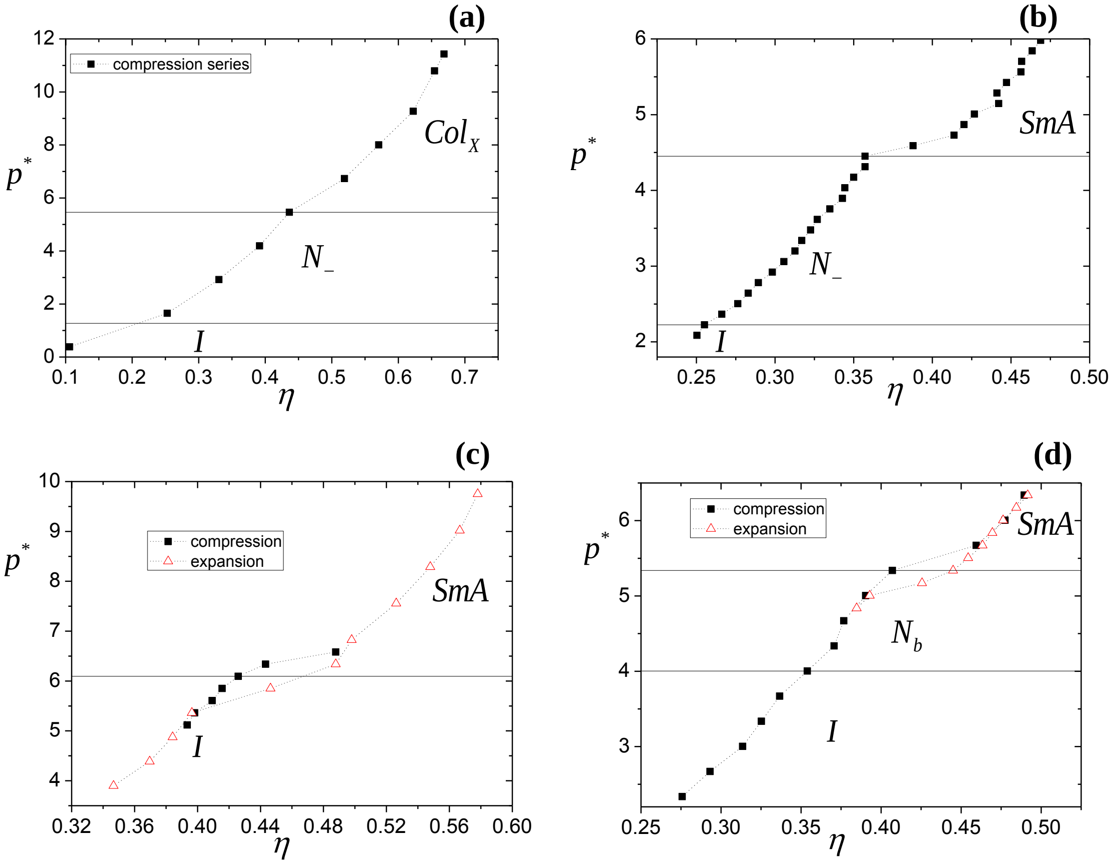

Fig. S2. Equations of state for systems consisting of SP particles (a) $\left(w^*, l^*\right)=(11,12)$, (b) $\left(w^*, l^*\right)=(4,12)$, (c) $\left(w^*, l^*\right)=(3,9)$ and (d) $\left(w^*, l^*\right)=\left(\sqrt{11}, 11\right)$. The solid symbols correspond to EOS calculated from compression runs from well equilibrated low-density isotropic states and the open symbols are EOS obtained by expansion from close packed states. The density jump accompanying the $N-I$ phase transition is rather small in comparison with the corresponding jump along the $N-Sm$ and $I-Sm$ phase transitions.

S3. Cubatic phase for two representative $\left(w^*,l^*\right)$ molecular geometries.

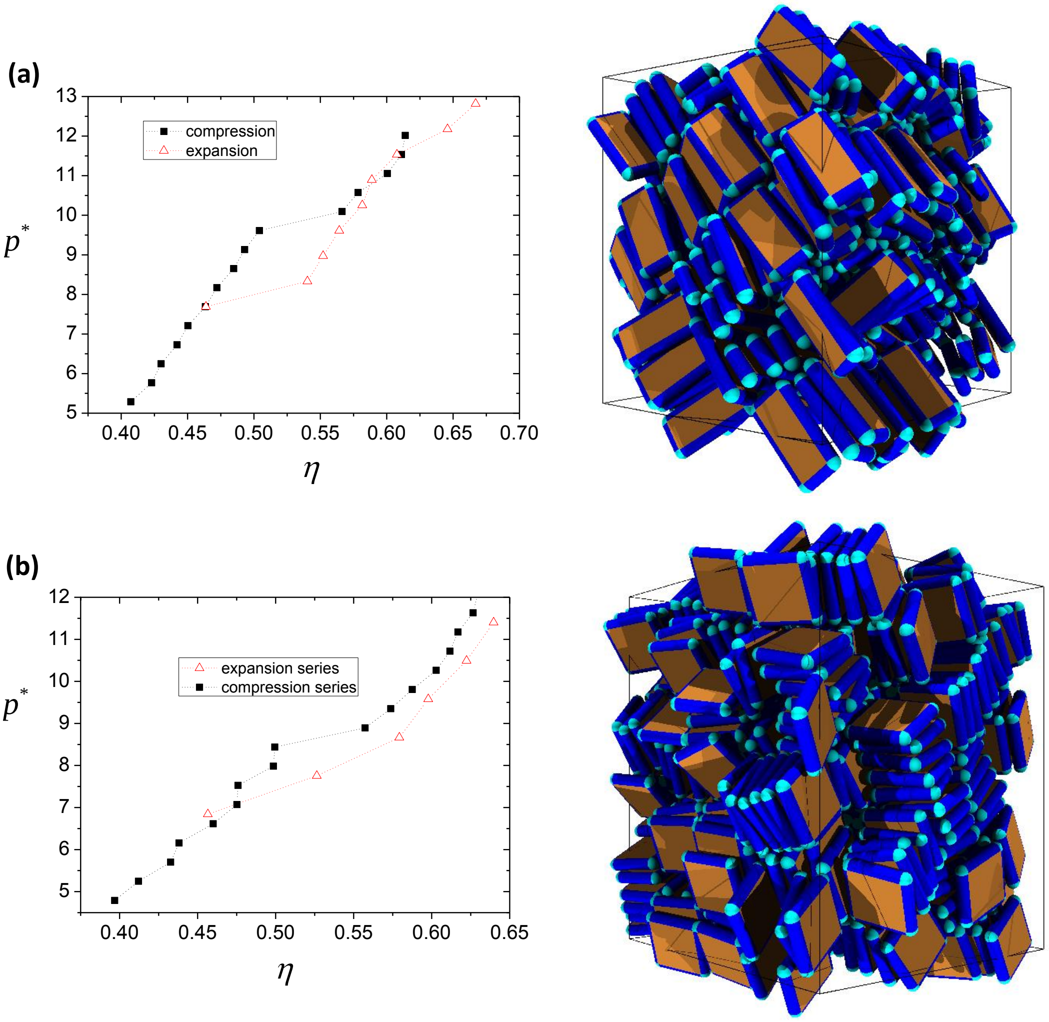

Fig. S3. Equations of state (pressure vs packing fraction) and representative snapshots of cubatic phases for systems consisting of SP particles with (a) $\left(w^*,l^*\right)=(3,6)$ and (b) $\left(w^*,l^*\right)=(5,5)$. The solid and open symbols correspond to compression and expansion runs respectively. The snapshot in (a) corresponds to $p^*=11.54$ and indicates the formation of well defined stacks of particles forming short biaxial columns or Smectic-like clusters, while in (b) the particles form short uniaxial columns. In both cases the nematic-like orientational correlations diminish after a few molecular lengths.

Note that the relative stability of the cubatic phases with respect to SmA and/or the Columnar phase is still an open issue. For a detailed discussion see refs[1-3].

REFERENCES

[1] M. Marechal, A. Patti, M. Dennison, and M. Dijkstra. Frustration of the Isotropic-Columnar Phase Transition of Colloidal Hard Platelets by a Transient Cubatic Phase *Phys. Rev. Lett.*, 2012, 108, 206101.

[2] M. R. Wilson, P. D. Duncan, M. Dennison and A. J. Masters. Molecular dynamics simulation studies of platelets with square cross-sectional area: formation of a stable cubatic phase. *Soft Matter*, 2012, 8, 3348-3356.

[3] P. D. Duncan, A. J. Masters, and M. R. Wilson. Thermodynamic stability of the cubatic phase of hard cut spheres evaluated by expanded ensemble simulations. *Phys. Rev.* E 2011, **84**, 011702.