

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231667692>

Phase Behavior of Contact Lens–Like Particles: Entropy–Driven Competition between Isotropic –Nematic Phase Separation and Clustering

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JANUARY 2010

Impact Factor: 7.46 · DOI: 10.1021/jz900448e

CITATIONS

13

READS

37

2 AUTHORS:



Giorgio Cinacchi

Universidad Autónoma de Madrid

60 PUBLICATIONS 557 CITATIONS

SEE PROFILE



Jeroen S van Duijneveldt

University of Bristol

72 PUBLICATIONS 1,518 CITATIONS

SEE PROFILE

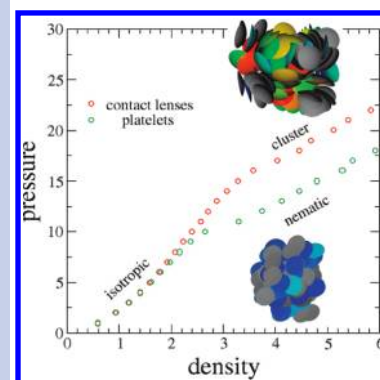
Phase Behavior of Contact Lens-Like Particles: Entropy-Driven Competition between Isotropic–Nematic Phase Separation and Clustering

Giorgio Cinacchi* and Jeroen S. van Duijneveldt

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England

ABSTRACT The novel phase behavior of hard partial spherical surfaces is reported, focusing on particles close to the platelet limit, similar to contact lenses. Spherical caps of sufficiently large radius of curvature exhibit a transition from the isotropic to the nematic discotic phase. By reducing the radius further, however, the latter phase is no longer stable, and the isotropic phase evolves into a different phase characterized by the simultaneous aggregation of the centers of the parent spheres and the organization of the concave particles on the corresponding and interpenetrating spherical surfaces. Contact lens-like particles thus exhibit a competition between a fluid–fluid phase transition and a clustering phenomenon, similar to what is observed in colloidal suspensions forming cluster phases or molecular systems forming micelles. For contact lens-like particles, however, this competition does not involve any energetic contribution and is purely entropy driven.

SECTION Macromolecules, Soft Matter



The basic model to study the phase behavior and properties of discotic liquid crystals is the hard, rigid and infinitely thin disk. These particles have no volume but exclude a finite volume toward one another. On increasing density, they exhibit a transition from the isotropic to the discotic nematic phase. This phase behavior was reported long ago.^{1,2} Nevertheless, hard platelets are still of much currency (e.g., refs 3–5). In this Letter, a more general model is considered. It consists of hard partial spherical surfaces of finite radius R . By varying R and constraining the surface area of one side to a certain value, σ^2 , one obtains rigid and infinitely thin particles covering the entire range from hard platelets to hard spheres. Except for these two limits, the particles of this class are concave. This is of interest, as the great majority of theoretical and simulational studies performed to date on the phase behavior and properties of hard particles concern convex particles.⁶

In addition, partial spherical surfaces can be considered as elementary models for a variety of experimental systems: (i) Bowlic liquid crystals. Thermotropic examples of these mesogens were synthesized a few decades ago, with the intention to generate ferroelectric phases,^{7–11} and a computer simulation study using a generic model including attractive interactions has been recently performed.¹² (ii) Buckybowlic molecules.^{13–17} These are obtained by excising a fragment of the C_{60} fullerene molecule and saturating the dangling bonds with hydrogen atoms. If the number of carbon atoms in the resulting molecule is sufficiently large, the molecule is curved. There is an increasing interest in buckybowlic molecules for a variety of reasons.^{13,17} Similarly to any polynuclear aromatic hydrocarbon, dispersion and electrostatic interactions will

play a role in determining their phase behavior and properties. Still, partial spherical surfaces may be viewed as a minimal model for them. (iii) Suspensions of colloidal particles, which can be prepared with a spectrum of shapes, sizes, and customized properties.¹⁸ Indeed, bowlic colloidal particles, resembling the object generated by a revolving crescent, have been prepared very recently, and their self-assembling properties have been studied. These experimental investigations were accompanied by computer simulations on model hard particles of the same type, within the range from the infinitely thin hemisphere to the half-sphere. Several columnar and crystalline phases were predicted at high density (Marechal et al., unpublished results).

The present work focuses on particles close to the hard platelet limit and in the low density regime. Systems of hard partial spherical surfaces were simulated by the Monte Carlo (MC) method in the isothermal–isobaric ensemble.^{19,20} The overlap criterion used is consistent with that described in ref 21 and reproduces the overlap criteria for hard platelets and hard spheres in the respective limits. Several values of R were considered, keeping the surface area of each particle side equal to σ^2 : from $R^* = R/\sigma \rightarrow \infty$, i.e., hard platelets of diameter $D/\sigma = 2/\sqrt{\pi}$ to $R^* = 1$, i.e., contact lens-like particles. Exploratory runs were performed with a number of particles $N = 125$. Extensive runs were performed with $N = 512$ or 1000. For each state point, identified by a value of pressure

Received Date: December 23, 2009

Accepted Date: January 25, 2010

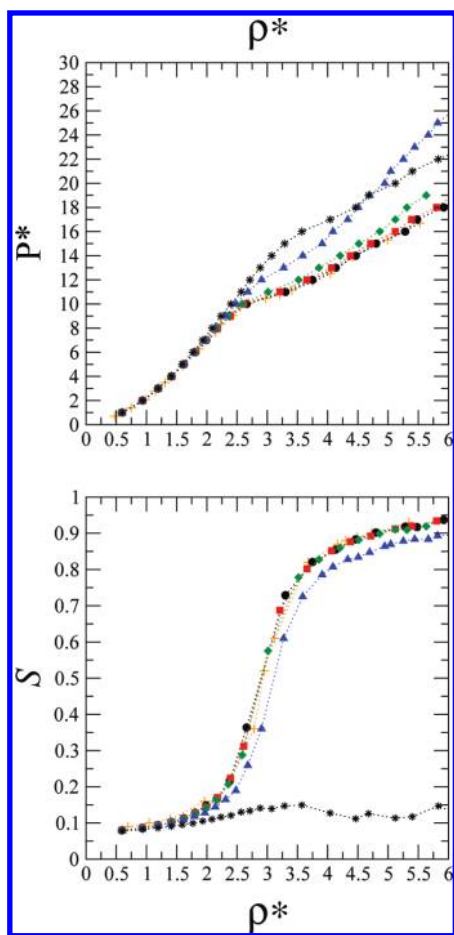


Figure 1. EOS (top) and nematic orientational order parameter (bottom) of partial spherical surfaces: $R^* = 100$ (circles), $R^* = 10$ (squares), $R^* = 5$ (diamonds), $R^* = 2$ (triangles), $R^* = 1$ (asterisks). The corresponding data from ref 2 are also given (plusses).

$P^* = P\sigma^3/k_B T$, simulations were started either from a low density isotropic configuration, a higher density perfectly oriented columnar configuration, or a configuration from a nearby state point. The equilibration runs took a minimum of 100 MC kcycles. No dependence on the starting configuration was seen, with all separate runs converging to the same value of density at a given pressure. Production runs took a minimum of 300 MC cycles. Each MC cycle consisted of N attempts to translate a randomly selected particle, N attempts to rotate a randomly selected particle, an inversion move in which the unit vector $\hat{\mathbf{u}}$ of a randomly selected particle is tentatively reversed while maintaining the position of the pole, and one attempt to change the length of a randomly selected edge of the cuboidal computational box.

Figure 1 shows the equation of state (EOS) obtained for several values of R^* , together with the graph of the nematic order parameter S .²² For $R^* > 1$, the behavior of both is consistent with the formation of a discotic nematic phase from an isotropic phase. For $R^* \geq 100$, the EOS is essentially indistinguishable from that of hard platelets.^{1,2,23} Reducing R^* , while the EOS in the isotropic phase remains the same, it progressively increases in the discotic nematic phase. This is

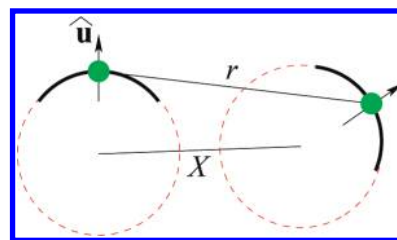


Figure 2. Illustration of symbols used in the text: $\hat{\mathbf{u}}$ is the unit vector along the direction joining the center with the pole of a partial spherical surface; r is the distance between the poles of two partial spherical surfaces; X is the distance between the centers of the respective underlying spheres.

not surprising, since curving a particle may be crudely equivalent to expanding its (excluded) volume.

For $R^* = 1$, however, such an increase of pressure appears no longer sustainable, and the contact lenses spontaneously organize differently. The change of slope of the EOS indicates that a phase transition occurs at density $\rho^* = \rho\sigma^3 \sim 3$ and $P^* \sim 14$. The value of $dP^*/d\rho^*$ in the higher pressure phase is close to 3, as is the case in the discotic nematic phase of hard platelets.^{1,2} However, the nematic order parameter is not a good descriptor of this transformation: it remains at values typical for a finite size isotropic system. Instead, in the higher pressure phase, the centers of the spheres, to which the caps belong, tend to cluster, and the contact lens-like particles tend to occupy the same spherical surface. Because the particles have no volume, these spherical surfaces are partially interpenetrating.

This phenomenon can be appreciated by examining the pair correlation functions, $g_n(r)$, of the unit vector, $\hat{\mathbf{u}}$, pointing from the center of the underlying sphere to the pole of the partial spherical surface and the pair correlation function, $G(X)$, of the centers of the underlying spheres (Figure 2).

The orientational pair correlation functions are defined as

$$g_n(r) = \left\langle \frac{\sum_{i=1}^N \sum_{j \neq i}^N \delta(r - r_{ij}) P_n(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)}{\sum_{i=1}^N \sum_{j \neq i}^N \delta(r - r_{ij})} \right\rangle \quad (1)$$

with P_n being the n th Legendre polynomial, r_{ij} being the distance between the poles of particles i and j , having orientations $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$, respectively, and the angular brackets signifying an average over configurations.

The positional pair correlation function $G(X)$ is defined as

$$G(X) = \frac{1}{N} \left\langle \frac{1}{\rho^*} \sum_i^N \sum_{j \neq i}^N \delta(X - X_{ij}) \right\rangle \quad (2)$$

with X_{ij} being the distance between the centers of the spheres underlying particle i and j and the angular brackets signifying an average over configurations.

The functions $g_n(r)$ measure the orientational correlation between two particles separated by a distance r (Figure 3). On increasing P^* , the value of these functions at $r \sim 0$ increases. This tendency for column formation is to be expected for discoidal objects. Yet, the functions $g_n(r)$ all decay to zero, which means that there is no tendency to form a long-range

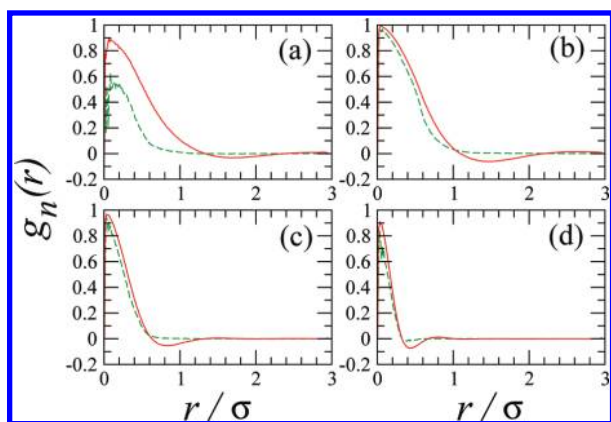


Figure 3. (a) $g_1(r)$; (b) $g_2(r)$; (c) $g_4(r)$; (d) $g_8(r)$. In panels a–d, the green dashed curve refers to $P^* = 13$, while the red solid curve refers to $P^* = 19$. All curves refer to $R^* = 1$.

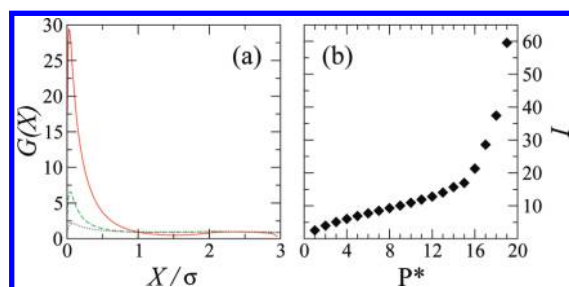


Figure 4. (a) The function $G(X)$ at $P^* = 7$ (black dotted line), $P^* = 13$ (green dashed line), and $P^* = 19$ (red solid line). (b) The quantity I as a function of P^* . All data refer to $R^* = 1$.

columnar structure. Closer inspection reveals a qualitative change. For $P^* < 14$, the g_n functions, with n being even, decay to zero monotonically, whereas for $P^* > 14$ they decay to zero in an oscillatory fashion. The fact that $g_4(r)$ decays oscillatorily to zero excludes the possibility that the higher pressure phase is cubic. This phase has been observed in systems of cut spheres.²⁴ If one associates the diameter of the base and the height of the present contact lens-like particle with, respectively, the diameter and thickness of a cut-sphere particle, the aspect ratio of the resulting cut sphere would be 0.147, close to the range of aspect ratios, [0.15;0.3], for which a cubic phase has been observed.^{24,25} For a cubic phase, however, the functions $g_4(r)$ and $g_8(r)$ should be long-ranged.²⁴

The oscillatory decay of the g_n functions originates in the tendency of the contact lens-like particles to reside on the same spherical surface, which is consistent with the tendency of the parent spheres to cluster. This is illustrated in Figure 4a, showing the function $G(X)$ for three values of pressure. For $P^* = 7$ and $P^* = 13$, $G(X)$ has a moderate structure, rapidly reaching the limiting value of unity. For $P^* = 19$, the peak that $G(X)$ exhibits around $X = 0$ is significantly increased. Figure 4b provides, as a function of pressure, the value of the integral I , defined as

$$I = 4\pi\rho \int_0^\sigma dXX^2G(X) \quad (3)$$

which measures the number of particles having the center of the underlying sphere comprised in the interval $[0;\sigma]$ from

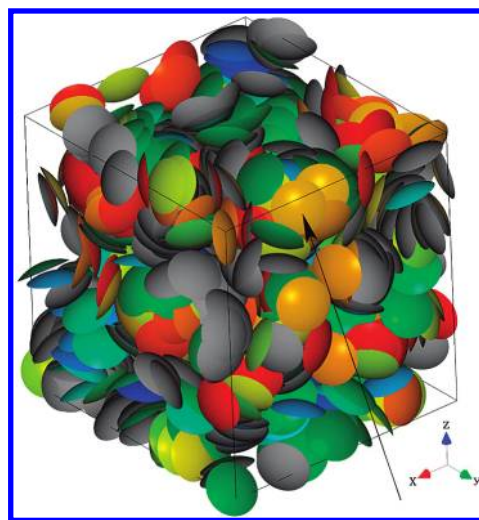


Figure 5. Snapshot of a configuration of contact lens-like particles, $R^* = 1$, generated during an MC run conducted at $P^* = 19$. The arrow indicates an example of groups of particles that tend to organize around the same spherical surface.

the center of the underlying sphere of a reference contact lens-like particle. The increase of I for $P^* > 14$ suggests that the transition to the cluster phase is very weak or indeed continuous.

Figure 4 shows that, in the cluster phase, the centers of the spheres sustaining the contact lenses tend to coincide. Hence, the concave particles tend to self-assemble on the same spherical surface. This dictates specific correlations among the orientations of the particles, which ultimately determine the oscillatory decay of g_n . For instance, particles sharing the same sphere center, but whose poles are separated by a distance 2σ , must be antiparallel. This is reflected in the rise of g_2 around this distance.

Figure 5 provides a snapshot of a typical configuration at $P^* = 19$, created with the program QMGA.^{26,27} The full range of colors observable reflects the global orientationally isotropic character of the higher pressure phase. Yet, groups of contact lens-like particles can be recognized, which tend to organize into short stacks and, more importantly, around the same spherical surface.

The aggregation of these concave particles resembles the formation of cluster phases in colloidal systems with competing interactions (e.g., refs 28–30): short-range attraction associated with a long-range repulsion. The changes in the phase behavior with curvature of the present particles also exhibit similarities with molecular systems that show a competition between a fluid–fluid phase separation and micellization, e.g., telechelic star copolymers.³¹

Remarkably, in the case of contact lens-like particles, this phenomenology is purely entropy driven. Contrary to the above-mentioned systems, the clustering does not involve any energetic contribution. Rather, it should arise from a competition between the roundness of the particles and the flatness of the three-dimensional space.

Further aspects of the phase behavior and properties of these intriguing concave particles will be considered in the near future. On increasing the pressure more, a translationally

ordered structure, columnar or crystalline, might intervene, but this is not expected until very high pressure as the particles have no volume. It may be opportune to reiterate that the cluster phase is obtained both starting from an isotropic phase and an initially perfect columnar phase and that no other phase was found to be mechanically stable in the upper part of the range of pressure values here investigated. One additional aspect very worth investigating is whether, at much higher pressure, the clusters of contact lens-like particles in turn organize at the sites of a regular lattice (e.g., ref 32).

Completely open is the question of whether and how a similar phase behavior could be observed in appropriate real experimental systems. One potential issue with this is that any real particle has a finite volume and this might inhibit the formation of a high density fluidlike phase while favoring the formation of a translationally ordered phase. In addition, the novel cluster phase appears hard to detect with conventional techniques customarily used for orientationally ordered phases. Presently, it would seem that only a scrupulous examination of the EOS in the fluid branch might reveal the existence of the predicted phase behavior. In this respect, the recently reported deformable thin gel disks³³ would appear to be promising candidates for the preparation of real contact lens-like particles. Once the techniques developed there are extended to the colloidal domain, the phase behavior and properties of suspensions of real contact lens-like particles could be investigated.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: giorgio.cinacchi@bristol.ac.uk.

ACKNOWLEDGMENT This research is supported by the European Commission via a Marie Curie Intra-European Research Fellowship, project number PIEF-GA-2007-220557. Special thanks are due to Adrian Gabriel and Guido Germano (University of Marburg) for having incorporated the partial spherical surfaces in their visualization program QMGA, and Paddy Royall (University of Bristol) for the critical reading of the manuscript. M. Marechal and the other authors (University of Utrecht) of the work entitled Phase Behavior and Structure of a New Colloidal Model System of Bowl-Shaped Particles are thanked for a preprint.

REFERENCES

- Frenkel, D.; Eppenga, R. Monte Carlo Study of the Isotropic–Nematic Transition in a Fluid of Thin Hard Disks. *Phys. Rev. Lett.* **1982**, *49*, 1089–1092.
- Eppenga, R.; Frenkel, D. Monte Carlo Study of the Isotropic and Nematic Phases of Infinitely Thin Hard Platelets. *Mol. Phys.* **1984**, *52*, 1303–1334.
- Esztermann, A.; Reich, H.; Schmidt, M. Density Functional Theory for Colloidal Mixtures of Hard Platelets, Rods and Spheres. *Phys. Rev. E* **2006**, *73*, 011409.
- Harnau, L. Structure and Thermodynamics of Platelet Dispersions. *Mol. Phys.* **2008**, *106*, 1975–2000.
- Cheung, D. L.; Anton, L.; Allen, M. P.; Masters, A. J.; Phillips, J.; Schmidt, M. Structure and Stability of Isotropic States of Hard Platelet Fluids. *Phys. Rev. E* **2008**, *78*, 041201.
- Allen, M. P.; Evans, G. T.; Frenkel, D.; Mulder, B. Hard Convex Body Fluids. *Adv. Chem. Phys.* **1993**, *86*, 1–166.
- Malthete, J.; Collet, A. Inversion of the Cyclotriphenylene Cone in a Columnar Mesophase - A Potential Way to Ferroelectric Materials. *J. Am. Chem. Soc.* **1987**, *109*, 7544–7545.
- Cornetti, G.; Dalcanale, E.; Du Voxel, A.; Levelut, A. M. New Bowl-Shaped Columnar Liquid Crystals. *J. Chem. Soc. Chem. Commun.* **1990**, 163–165.
- Cornetti, G.; Dalcanale, E.; Du Voxel, A.; Levelut, A. M. A New, Conformationally Mobile Macrocyclic Core for Bowl-Shaped Columnar Liquid Crystals. *Liq. Cryst.* **1992**, *11*, 93–100.
- Xu, B.; Swanger, T. M. Rigid Bowl-Like Liquid Crystals Based on Tungsten-Oxo Calix[4]arenes: Host-Guest Effects and Head-To-Tail Organization. *J. Am. Chem. Soc.* **1993**, *115*, 1159–1160.
- Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. Stacking of Conical Molecules with a Fullerene Apex into Polar Columns in Crystals and Liquid Crystals. *Nature* **2002**, *419*, 702–705.
- Berardi, R.; Ricci, M.; Zannoni, C. Columnar Liquid Crystals formed by Bowl-Shaped Mesogens. A Monte Carlo Study. *Soft Matter* **2008**, *4*, 2030–2038.
- Rapideau, P. W.; Sygula, A. Buckybowls: Polynuclear Aromatic Hydrocarbons related to the Buckminsterfullerene Surface. *Acc. Chem. Res.* **1996**, *29*, 235–242.
- Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. Crystallographic Characterization of the Molecular Structure and Solid State Packing of the Fullerene-Shaped Hydrocarbon C₃₆H₁₂. *J. Am. Chem. Soc.* **1997**, *119*, 5766–5767.
- Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. Creation of Hoop- and Bowl-Shaped Benzenoid Systems by Selective Detraction of [60]Fullerene Conjugation. [10]Cyclophenacene and Fused Corannulene Derivatives. *J. Am. Chem. Soc.* **2004**, *126*, 8725–8734.
- Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. Structural Elucidation of Sumanene and Generation of its Benzylic Anions. *J. Am. Chem. Soc.* **2005**, *127*, 11580–11581.
- Kawase, T.; Kurata, H. Ball-, Bowl-, and Belt-Shaped Conjugated Systems and Their Complexing Abilities: Exploration of the Concave-Convex π - π Interaction. *Chem. Rev.* **2006**, *106*, 5250.
- Glotzer, S. C.; Solomon, M. J. Anisotropy of Building Blocks and Their Assembly into Complex Structures. *Nat. Mater.* **2007**, *6*, 557–562.
- Wood, W. W. Monte Carlo Calculations for Hard Disks in the Isothermal–Isobaric Ensemble. *J. Chem. Phys.* **1968**, *48*, 415–434.
- King, H. F. Isobaric versus Canonical Ensemble Formalism for Monte Carlo Studies of Liquids. *J. Chem. Phys.* **1972**, *57*, 1837–1841.
- He, M.; Siders, P. Monte Carlo Calculation of Orientationally Anisotropic Pair Distributions and Energy Transfer in a Model Monolayer. *J. Phys. Chem.* **1990**, *94*, 7280–7288.
- The nematic order parameter, S , has been calculated as usual by constructing the matrix

$$Q_{a,b} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} u_{i,a} u_{i,b} - \frac{1}{2} \delta_{a,b} \quad (4)$$

with $u_{i,a}$ being the a th component of the unit vector $\hat{\mathbf{u}}$ describing the orientation of particle i and $\Delta_{a,b}$ being the Kronecker symbol, taking the largest eigenvalue, s_{max} , the corresponding eigenvector being identified with the director, and averaging s_{max} over the configurations generated during an MC run.

- (23) Note that the unit of length in refs 1 and 2 is the platelet diameter, which differs from the present unit of length by a factor of $2/\sqrt{\pi}$.
- (24) Veerman, J. A. C.; Frenkel, D. Phase Behavior of Disklike Hard-Core Mesogens. *Phys. Rev. A* **1992**, *45*, 5632–5648.
- (25) Duncan, P. D.; Denninson, M.; Masters, A. J.; Wilson, M. R. Theory and Computer Simulation for the Cubatic Phase of Cut Spheres. *Phys. Rev. E* **2009**, *79*, 031702.
- (26) Gabriel, A. T.; Meyer, T.; Germano, G. Molecular Graphics of Convex Body Fluids. *J. Chem. Theory Comp.* **2008**, *4*, 468–476.
- (27) <http://qmgm.sourceforge.net>.
- (28) Groenewold, J.; Kegel, W. K. Anomalous Large Equilibrium Clusters of Colloids. *J. Phys. Chem. B* **2001**, *105*, 11702–11709.
- (29) Sciortino, F.; Mossa, S.; Zaccarelli, E.; Tartaglia, P. Equilibrium Cluster Phases and Low-Density Arrested Disordered States: The Role of Short-Range Attraction and Long-Range Repulsion. *Phys. Rev. Lett.* **2004**, *93*, 055701.
- (30) Fernandez Toledano, J. C.; Zaccarelli, E.; Sciortino, F. Colloidal Systems with Competing Interactions: From an Arrested Repulsive Cluster Phase to a Gel. *Soft Matter* **2009**, *5*, 2390–2398.
- (31) Lo Verso, F.; Panagiotopoulos, A. Z.; Likos, C. N. Aggregation Phenomena in Telechelic Star Polymer Solutions. *Phys. Rev. E* **2009**, *79*, 010401(R).
- (32) de Candia, A.; Del Gado, E.; Fierro, A.; Sator, N.; Tarzia, M.; Coniglio, A. Columnar and Lamellar Phases in Attractive Colloidal Systems. *Phys. Rev. E* **2006**, *74*, 010403(R).
- (33) Klein, Y.; Efrati, E.; Sharon, E. Shaping of Elastic Sheets by Prescription of Non-Euclidean Metrics. *Science* **2007**, *315*, 1116–1120.