

Assembly of porous smectic structures formed from interlocking high-symmetry planar nanorings

Carlos Avendaño^a, George Jackson^b, Erich A. Müller^b, and Fernando A. Escobedo^c

^aSchool of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester M13 9PL, UK; ^bDepartment of Chemical Engineering, Centre for Process Systems Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK; ^cSchool of Chemical and Biomolecular Engineering, 120 Olin Hall, Cornell University, Ithaca, New York 14853, USA.

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Materials comprising porous structures, often in the form of interconnected concave cavities, are typically assembled from convex molecular building blocks. The use of nanoparticles with a characteristic non-convex shape provide a promising strategy to create new porous materials, an approach that has been recently employed with cage-like molecules to form remarkable liquids with “scrabbled” porous cavities [Giri, N. et al. (2015) *Nature* 527:216]. Nonconvex mesogenic building blocks can be engineered to form unique self-assembled open structures with tunable porosity and long-range order that is intermediate between that of isotropic liquids and of crystalline solids. Here we propose the design of highly open liquid-crystalline structures from rigid nanorings with unique classes of geometry. By exploiting the entropic ordering characteristics of athermal colloidal particles [Allen, M. P., Evans, G. T., Frenkel, D., Mulder, B. (1993) *Adv. Chem. Phys.* 86:1], we demonstrate that high-symmetry nonconvex rings with large internal cavities interlock within a two-dimensional layered structure leading to the formation of distinctive liquid-crystalline smectic phases. We show that these novel smectic phases possess uniquely high free volumes of up to ~95%, a value significantly larger than the 50% that is typically achievable with smectic phases formed by more conventional convex rod- or disc-like mesogenic particles.

Nanorings | Self-assembly | Non-Convex particles |

Self assembly of particles ranging in size from the nanometer to the micrometer scales can be used to fabricate structures in the mesoscale regime [1–5], otherwise difficult to achieve with traditional methods of chemical synthesis. Strategies to produce functional materials from the self assembly of relatively simple non-spherical (anisotropic) building blocks have undergone unprecedented growth as a result of recent advances in experimental techniques to fashion colloidal and nanoparticles of arbitrary shape and well-defined sizes [6–9]. An appealing feature of colloidal particles is that the repulsive and attractive contributions of the interaction between the particles can be modulated by controlling the properties of both the particle surface and the solvent medium to induce different types of forces, including short-range repulsions approaching hard-core (athermal) interactions [10].

Colloidal particles are commonly represented using simplified coarse-grained convex geometries including ellipsoids, spherocylinders, polyhedra, and cut spheres [11, 12]. The phase behaviour of these convex models has been studied extensively by theory and simulation [13, 14]. Non-convex (NC) models have received significantly less attention. NC particles offer new possibilities for the fabrication of functional materials as a result of the self assembly of unique structures driven by interlocking and entanglement [15–20]. As featured in our current paper, NC particles can be packed into exotic highly

open (low-density) structures. Self-assembled NC frame-like arrays are of particular interest due to their unusual optical, electrical, and mechanical properties, as a consequence of the large surface-to-volume ratios that can be attained with NC particles. These emerging materials offer promise in a broad range of applications including drug delivery and therapeutics [18, 21–23], novel materials for catalysis [24], optics [18, 21], photonics [22, 23], and as nanopatterned scaffolds [25, 26].

Notwithstanding the potential of such materials, the experimental assessment of the different variables affecting the synthesis and characterization of NC particles is a thankless empirical task, particularly if one considers the limited range of stability of some of the more promising liquid-crystalline phases. Molecular simulation plays an invaluable role in reducing the experimental effort providing a direct link between the geometry of the constituent particles and the final microstructures adopted by the material.

We present a comprehensive investigation of the structures formed by a particular class of frame-like particles, namely colloidal rings, by direct molecular simulation. The nanorings are taken to be planar and perfectly rigid. Two geometries are investigated starting from a circular shape as the basis: ellipsoidal and polygonal rings. Our model particles are represented as a number of N_b tangent spherical segments of diameter σ forming a planar ring interacting via repulsive interactions. The diameter of each bead is much smaller than the characteristic dimensions of the particles, allowing the beads to be distributed in space to form circular rings of different diameters, rings of different ellipticity, polygons of various symmetries, and thick-walled open cylindrical structures resembling doughnuts, bands, and washers.

More specifically, three types of circular and equilateral

Significance Statement

The formation of low-density porous structures is currently a topic of significant interest due to the advantageous electrical, optical, and chemical properties of the materials. We have observed the formation of unique highly open liquid-crystalline smectic phases formed by the interlocking of highly symmetrical planar nanorings. In particular, we demonstrate the relationship between the size of the internal cavity of the rings and their symmetry on the formation of stable liquid-crystalline phases with free volume up to 95%.

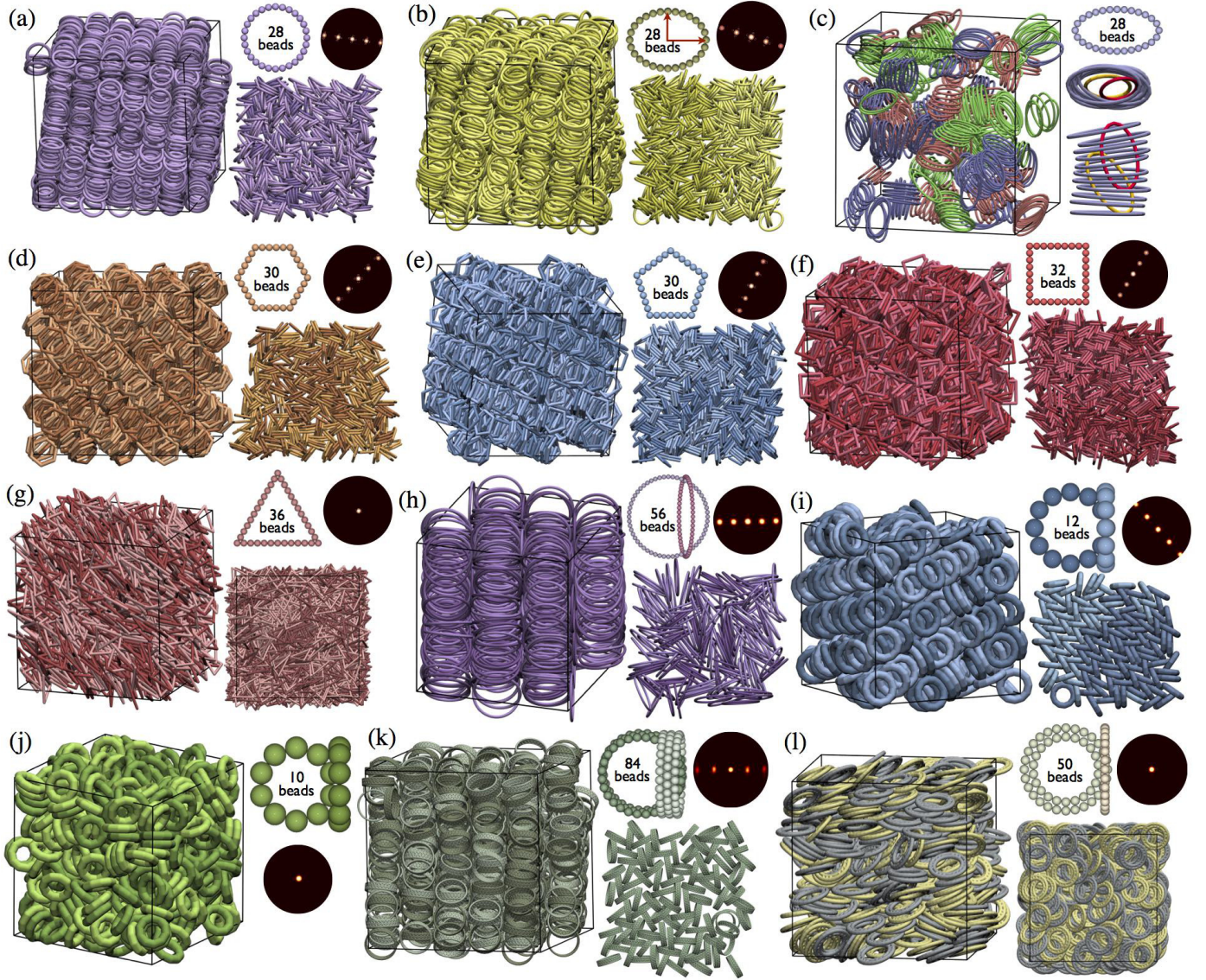


Fig. 1. Particle models and stable microstructures observed in colloidal nanorings of various geometry. Figures (a)-(g) represent the structures exhibited by rings of different symmetry but with a similar planar area: (a) smectic-A (SmA) phase for circular rings ($N_b = 28$); (b) SmA phase for ellipsoidal rings ($N_b = 28$) with an aspect ratio of $e = 0.85$; (c) disordered phase for ellipsoidal rings ($N_b = 28$) with $e = 0.5$ exhibiting clustered domains of tubular morphology (only clusters of more than three particles are shown); (d) and (e) SmA phases for hexagonal and pentagonal rings ($N_b = 30$), respectively; (f) SmA phase for square rings ($N_b = 32$); and (g) nematic (N) phase for triangular rings ($N_b = 36$). In each case we present a single particle with the corresponding number of beads, a snapshot of the liquid-crystalline structure, and a single layer of the SmA phase or a N phase observed along the director. Figures (h)-(j) correspond to the phases observed in circular rings of type I (doughnuts). These systems correspond to rings of increasing thickness: (h) $N_b = 56$ beads; (i) $N_b = 12$ beads; and (j) $N_b = 10$ beads. Systems (h) and (i) are both seen to form SmA phases; by contrast system (j), corresponding to a system with non interpenetration ($\chi = 0$), is isotropic (I) and does not form an ordered fluid structure. (k) corresponds to the SmA phase formed by multi-stacked cylindrical rings of type II (bands) comprising three layers. (l) corresponds to the N phase formed by circular rings of type III (washers) comprising one inner layer. For each system in Figures (h)-(l) two particles are depicted to help visualize the maximum possible interpenetration. The static structure factor $S(\mathbf{k})$ projected in a plane containing the director of the system is shown for all systems. The low wave-vector $S(\mathbf{k})$ for systems (a), (b), (d-f), (h), (i), and (k) is characterized by strong unidimensional signals due to the formation of SmA layers.

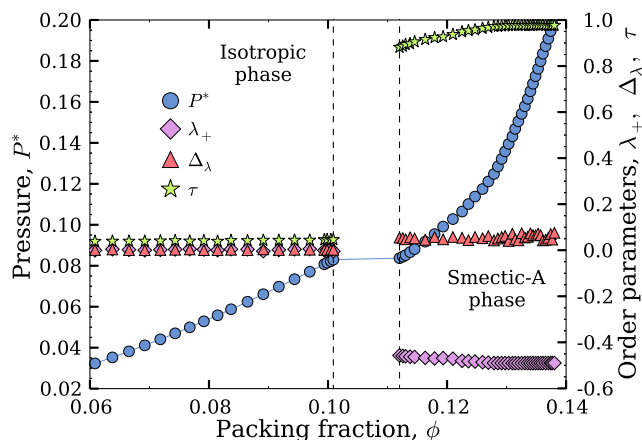


Fig. 2. Pressure-packing fraction (P^* - ϕ) phase diagram for circular colloidal nanorings with $N_b = 28$ beads. The dependence of the nematic λ_+ , biaxial Δ_λ , and layering τ order parameters (defined in the Methods Section) on the packing fraction ϕ is indicated.

polygonal rings are modelled by systematically varying the symmetry, the cavity size, and the width of the rings: type-I single rings (doughnuts) with different number of tangent beads N_b and symmetries (see Figure 1 (a-j)); type-II multi-stacked circular rings made up of n identical N_b rings bound sideways into cylindrical bands (see Figure 1(k)); and type-III multilayered circular rings made up of an N_b outer ring and n inner rings resembling washers (see Figure 1(l)).

Microstructures and Phase Boundaries

An example of the class of NC particles classified here as circular rings of type I is depicted in Figure 1(a). In contrast to the phases commonly associated with colloidal platelets and molecular discotics [27, 28], the circular-ring system does not form (discotic) nematic (N) or columnar (C) phases as a consequence of the large particle cavity. On sequential compression of a $N_b = 28$ bead ring system (see Figure 1 (a)) using isothermal-isobaric (NPT) molecular dynamics (MD), the system exhibits a first-order phase transition from an isotropic (I) liquid state at packing fraction $\phi \sim 0.10$ to a smectic-A (SmA) phase at $\phi \sim 0.11$ (see Figure 2). The SmA phase is characterised by the formation of layers along the director of the system $\hat{n}$, as confirmed by the large values of the positional (layering) order parameter τ in the direction of the layers. The ring particles are oriented perpendicular to the direction of the layers, and as a consequence the phase is characterized by negative values of the orientational (nematic) order parameter λ_+ . At the higher packing fractions, the order parameters take values of $\lambda_+ \sim -0.5$ and $\tau \sim 1.0$ revealing a high degree of perpendicular orientational order of the rings with respect to the director. Moreover, the low packing fractions reveals that the SmA phase is highly open due to the combined effect of the layered packing and large internal cavities of the particles as is apparent from Figure 1(a). The biaxial order parameter Δ_λ does not suggest long-range orientational order of the rings within the smectic layers, ruling out a biaxial phase. However, a close inspection of the clustering in the layers reveals that about 50% of the rings form small stack-like clusters consisting of 2 to 4 particles, with dimer clusters the more abundant. The exceptional

self assembly into this layered microstructure is driven by an interlocking process in which the ring particles, or small clusters, fill the cavities of neighbouring particles in order to pack more efficiently. The mean-square displacement (MSD) and its projections in the directions along and perpendicular to the director for the lowest-density SmA state can be employed to analyze the mobility of the particles. As is apparent from the analysis provided in the supplementary information (SI), the particles exhibit considerable mobility in their own layers with occasional hopping of particles to adjacent layers (not dissimilar to the dynamics of colloidal rods in smectic layered structures) ruling out dynamically arrested states [29].

To better understand the effect of the particle symmetry on the formation of SmA phases exhibited by circular rings, the shape of the rings can be deformed uniaxially into an ellipsoidal geometry. Our model ellipsoidal ring particles are characterized by the ratio of the minor and major axis $e = b/a$, and the number of beads forming the ring (which is kept fixed as $N_b = 28$). We analyze particles with different degrees of ellipticity: Figure 1(a), $e = 1.00$; Figure 1(b), $e = 0.85$; Figure 1(c), $e = 0.50$. The ring particles with an ellipticity of $e = 0.85$ form a SmA phase which is similar to that found for the circular rings (see Figure 1(a)). The I-SmA phase transition is shifted towards higher pressures and packing fractions relative to that of the circular rings; very long simulations are required to stabilize the SmA phase indicating that is more difficult to form the layered structure when the particle cavity is less symmetric. Indeed, for the particles with an ellipticity of $e = 0.50$, the formation of a mesophases is completely inhibited over the range of conditions explored, although the slow kinetics does not allow one to completely rule out a transition; disordered structures with large stack-like clusters are formed instead (see Figure 1(c)), so that the phase does not possess long-range orientational nor translational order. This suggests that the interlocking of particles is not sufficient to facilitate the layering into SmA phases; particles with high degrees of rotational symmetry are required to stabilize SmA layers of uniform thickness regardless of the orientation of the interlocking particles.

To further understand the role of the symmetry of the particle cavity in the stabilization of the liquid crystalline-phases, equilateral polygonal rings of type I of decreasing symmetry are also investigated: hexagonal, pentagonal, square, and triangular rings (see Figure 1(d-g)); the two-dimensional in-plane order of discrete rotational symmetry for these polygons is 6, 5, 4, and 3, respectively. Ring particles with hexagonal, pentagonal, and square symmetries are still found to exhibit a first-order transition from an I to a SmA phase. However, a reduction in the symmetry of the rings results in a diminished stability of the SmA phase with respect to the N phase, which is consistent with the behaviour observed for ellipsoidal rings. This reduced proclivity for self assembly can be inferred from the considerable increase in the transition pressure and the very long simulation runs required for the formation of the SmA phase, particularly in the case of square rings. It is also interesting to note that the discontinuity of the packing fraction at the transition becomes smaller, suggesting that the first-order nature of the phase transition becomes weaker as the particle symmetry is decreased. Both the nematic λ_+ and positional τ order parameters tend towards smaller values when the particle symmetry is decreased which is in line with

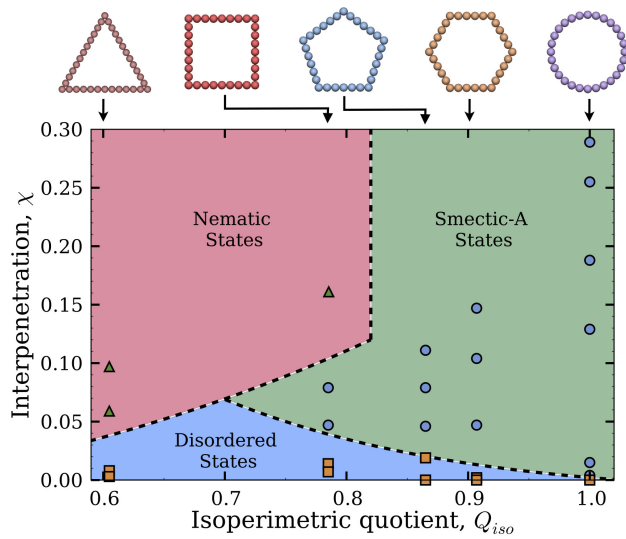


Fig. 3. Phase behaviour of colloidal polygonal nanorings of different symmetry (triangles, squares, pentagons, hexagons, and circular rings). The points represent stable nematic, smectic-A or disorder arrested states. The regions of stability are represented in terms of the degree of interpenetration χ and isoperimetric quotient Q_{iso} of the particles which characterize their symmetry.

the decreased stability of the SmA phases. An analysis of the MSD of the polygonal rings for the low-density smectic-A states (in the vicinity of the ordering transition) reveals that polygons, particularly in the case of squares, have a much lower mobility than circular rings; a comparison of the mobility at the same packing fraction reveals that the MSD is however comparable indicating that the particle dynamics is dominated by packing effects and is largely independent of the particle symmetry. It is also important to highlight that the concentration of trapped inter-layer particles, which can be considered as defects, increases when the symmetry of the particles is decreased. While these defects are almost absent in the SmA phase formed by circular rings (cf. SI), they are sufficiently abundant in the SmA phase of square rings to cover the entire area of the interlayer planes. As a consequence of the higher translational mobility of the interlayer particles compared to those in the smectic layers, the high interlayer concentration appears to be a factor in the stabilization of the SmA layers, compensating for the low rotational symmetry of the particles. A SmA phase is not formed in the case of triangular rings, the polygons with the lowest symmetry, and instead the system exhibits a N phase via a weak first-order transition from the I phase.

Having established that high-symmetry particles are ideal for the formation of the SmA phase with interlocking neighboring particles, we proceed to quantify how the extent of interlocking affects the viability of forming the smectic-A phase. For this purpose, it is convenient to define for the three types of ring, i.e., types I, II, and III, the degree of interpenetration χ as the ratio of the maximum number of beads N_{cross} of a given particle that can penetrate (cross) the cavity of another particle to the total number of beads N_b averaged over all accessible mutual orientations Ω : $\chi = \langle N_{cross}/N_b \rangle_{\Omega}$. Some examples of rings of the different types have already been depicted in Figure 1. In the case of type-I rings, the degree of interpenetration χ increases and the particle thickness δ

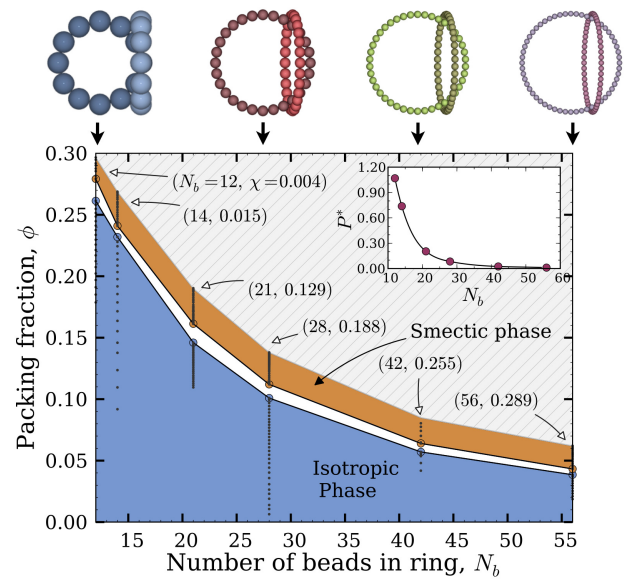


Fig. 4. Global phase diagram of circular colloidal nanorings of different bead thickness. The packing fraction ϕ of the I-SmA transition for models comprising different numbers of beads N_b and degrees of interpenetration χ , indicated in parentheses as (N_b, χ) . The simulated states are represented as black dots, and the grey hatched area represents thermodynamic states not studied. The transition pressure P^* for each system is indicated in the inset.

(relative to the ring diameter) decreases as the number of bead in the ring N_b is increased. For type-II cylindrical bands, χ decreases as n is increased because of the concomitant increase in δ (the cylinder height), while the cavity diameter remains constant. By contrast in the case of type-III rings (washers), χ decreases as the number of inner layers n is increased keeping δ constant.

The generic behaviour expected for polygonal rings of type I with different cavity sizes and particles symmetries, including those already described, is presented in Figure 3 indicating the regions of stability of the ordered phases (the reader is directed to the SI for further details). The cavity size and particle symmetry are characterized here in terms of the interpenetration parameter χ and the isoperimetric quotient Q_{iso} , defined as the ratio of the area of the ring to the area of a circle with same perimeter as the ring. Particles formed from $N_b \sim 12$ beads represents the lower bound of the cavity size for circular rings at which the SmA phase is observed, and is the smallest system with a non-zero value of χ where at least one bead can penetrate the cavity of a neighbouring particle. The microstructures formed by circular rings formed from various number of beads of increasing diameter are shown in Figure 1(h-j). One would expect the formation of a N phase for circular rings with $N_b < 12$, however, the small internal cavity of the rings appears to frustrate the alignment of the particles leading to the formation of dynamically arrested structures which lack long-range order and are essentially incompressible, and hypostatic, akin to the jammed phases observed in various anisotropic colloidal systems [30, 31] (cf. SI). A similar behaviour is observed for hexagonal and pentagonal rings for which SmA phases are observed only when the cavity is large enough. Interestingly, while square rings with small internal cavities exhibit SmA phases, systems of square rings with large cavities tend to form N phases instead. This further

demonstrates that square rings represent a lower-symmetry bound for the formation of SmA phases. Therefore, particles which possess both a high symmetry and a large internal cavity are likely candidates to form stable layered phases with a low packing fraction.

The role of the degree of interpenetration on the formation of liquid-crystalline phases, independently of the symmetry of the particles, is analyzed using circular rings of type I, II, and III. In the case of type-II ring cylindrical bands (see Figure 1(k)) with a thickness of two and three layers, corresponding to an interpenetrability of $\chi=0.134$ and 0.069 , respectively, the system still forms stable SmA phases, demonstrating the role of the degree of interpenetration for a fixed circular symmetry. Conversely, for type-III rings (washers), the incorporation of just a single inner layer reduces the size of the cavity enough to make the degree of interpenetration very small, promoting the formation of a N phase instead of a SmA phase (see Figure 1(l)).

Finally, the global phase diagram of type-I ring particles is shown in Figure 4 (see also Figure 1(a,h-j)), where it is apparent that the I-SmA phase transition shifts progressively to lower packing fractions for rings with increasingly open cavities (corresponding to a larger N_b , thinner δ , and larger χ). This is equivalent to the approach of the Onsager limit for infinitely long rods and infinitely thin platelets. In the case of the more traditional rod-like (calamitic) or disc-like (discotic) materials the transition from the N phase to the SmA or C phases occurs at packing fractions of 45-50% and is essentially insensitive to the aspect ratio [27, 32–34]. The second virial coefficient of a pair of freely rotating discs diverges in the limit of infinitely thin particles as the discs cannot interpenetrate [34]; though there is a degree of interpenetration the same is true of the infinitely thin rings. In the case of our NC nanoring particles, however, the packing fraction at the transition to the SmA phase decreases with increasing aspect ratio (increasing number of beads). For nanorings with the largest cavity studied, corresponding to $N_b = 56$, the I-SmA phase transition is exhibited at $\phi \sim 0.04$, and the transition density will decrease further for particles with larger cavities. *These low values of packing fraction suggest that colloidal nanoring particles offer promise in the formation of layered microstructures with very high porosity after drying of any solvent, corresponding to a free volume of 96% observed at high osmotic pressures.*

Conclusions

We have reported a detailed mapping for the formation of a distinctive class of self-assembled layered liquid-crystalline phases from colloidal nanorings in terms of both the symmetry of the particles and the degree of interpenetration. These highly porous structures are unique candidates as adsorption and storage materials due to both their large void volumes and fluidity [35]. One would expect a significant enhancement in the diffusivity of small particles within the smectic layers when compared with isotropic liquid phases of equivalent porosity. Inclusion compounds comprising these low-density layered structures could provide a route to additional control of the mechanical, optical, and electronic properties of the functional material.

Materials and Methods

The non-convex colloidal nanoring particles are modelled as a rigid necklace of N_b tangent spherical beads of diameter σ forming a planar structure. The beads interact via a soft repulsive WCA potential corresponding to the Lennard-Jones potential truncated and shifted to zero at the cut-off distance $r_c = 2^{1/6}\sigma$ [36, 37]. The principal orientation of a particle j is described with a unit vector $\hat{\mathbf{u}}_j$, which is perpendicular to the plane of the ring. The phase behaviour of the systems is obtained via compression, starting from low-density I states using MD simulation in the isobaric-isothermal (NPT) ensemble. Properties are reported in dimensionless units using the LJ parameters: pressure $P^* = P\sigma^3/(k_B T)$, temperature $T^* = k_B T/\epsilon$, time $t^* = t[\epsilon/(m\sigma^2)]^{1/2}$, and packing fraction $\phi = \pi N_b N \sigma^3/(6V)$, where k_B is the Boltzmann constant, ϵ is the well-depth of the untruncated LJ potential, m is the mass of the bead, N is the total number of ring particles, and V is the volume of the system. The nanorings are treated as perfectly rigid bodies, and the equations of motion are integrated using the leap-frog algorithm with a time step of $\delta t^* = 0.004$. To approximate the behaviour of hard particles, a temperature of $T^* = 1.25$ is set in all simulations [37, 38]. The temperature and pressure are controlled using a Nosé-Hoover thermostat and a Hoover barostat, respectively, for cubic simulation boxes with periodic boundary conditions in the three Cartesian coordinates [39, 40]. The simulations are carried out using DL_POLY software [41].

The orientational order of the system is characterized by computing the eigenvalues ($|\lambda_+| > |\lambda_0| > |\lambda_-|$) of the orientational tensor $\mathbf{Q}$ from the particle orientation vectors $\hat{\mathbf{u}}_j$; the director of the system $\hat{\mathbf{n}}$ corresponds to the eigenvector with the largest absolute eigenvalue λ_+ , the nematic order parameter [12]. The biaxial order, indicating particle orientations perpendicular to the main director, is analyzed using the difference of the eigenvalues associated with the eigenvectors that are perpendicular to the main director, i.e., $\Delta_\lambda = |\lambda_0 - \lambda_-|$. The formation of smectic layers in the system is monitored using a one-dimensional translational order parameter [42] defined as $\tau(\mathbf{k}) = (1/N) \langle \left| \sum_{j=1}^N \exp(i\mathbf{k}_d \cdot \mathbf{r}_j) \right|^2 \rangle$, where $\mathbf{k}_d$ is the wave vector in the plane of the layers that maximizes τ , and $\mathbf{r}_j$ is the centre of mass of particle j . This parameter is the discrete one-dimensional analogue of the translational order metric reported by Torquato *et al.* [43] evaluated using the wave vector with the same phase offset as the layering of the smectic states. The smectic layers can also be characterized using the structure factor $S(\mathbf{k}) = (1/N) \left| \sum_{l,m=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_{lm}) \right|^2$, where $\mathbf{k}$ is a wave vector in the plane containing the director, and $\mathbf{r}_{lm}$ is the vector connecting the centres of mass of particles l and m .

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1. Velez OD, Lenhoff AM, Kaler EW (2000) A class of microstructured particles through colloidal crystallization. *Science* 287(5461):2240.
2. Whitesides GM, Boncheva M (2002) Beyond molecules: self-assembly of mesoscopic and macroscopic components. *Proc. Natl. Acad. Sci. USA* 99(8):4773.
3. Xia Y, Gates B, Li ZY (2001) Self-assembly approaches to three-dimensional photonic crystals. *Adv. Mater.* 13(6):409.
4. Grzelczak M, Vermant J, Furst EM, Liz-Marzán LM (2010) Directed self-assembly of nanoparticles. *ACS Nano* 4(7):3591.
5. Glotzer SC (2015) Assembly engineering: materials design for the 21st century. *Chem. Eng. Sci.* 121:3.
6. Kim JW, Larsen RJ, Weitz DA (2006) Synthesis of nonspherical colloidal particles with anisotropic properties. *J. Am. Chem. Soc.* 128(44):14374.
7. Glotzer SC, Solomon MJ (2007) Anisotropy of building blocks and their assembly into complex structures. *Nat. Mater.* 6(8):557.
8. Hernandez CJ, Mason TG (2007) Colloidal alphabet soup: monodisperse dispersions of shape-designed lithoparticles. *J. Phys. Chem. C* 111(12):4477.

9. Sacanna S et al. (2013) Shaping colloids for self-assembly. *Nat. Commun.* 4:1688.
10. Yethiraj A, van Blaaderen A (2003) A colloidal model system with an interaction tunable from hard sphere to soft and dipolar. *Nature* 421(6922):513.
11. Onsager L (1949) The effects of shape on the interaction of colloidal particles. *Ann. N.Y. Acad. Sci.* 51:627.
12. Allen MP, Evans GT, Frenkel D, Mulder B (1993) Hard convex body fluids. *Adv. Chem. Phys.* 86:1.
13. Escobedo FA (2014) Engineering entropy in soft matter: the bad, the ugly and the good. *Soft Matter* 10(42):8388.
14. Baule A, Makse HA (2014) Fundamental challenges in packing problems: from spherical to non-spherical particles. *Soft Matter* 10(25):4423.
15. de Graaf J, van Roij R, Dijkstra M (2011) Dense regular packings of irregular nonconvex particles. *Phys. Rev. Lett.* 107:155501.
16. Atkinson S, Jiao Y, Torquato S (2012) Maximally dense packings of two-dimensional convex and concave noncircular particles. *Phys. Rev. E* 86(3):031302.
17. Gravish N, Franklin SV, Hu DL, Goldman DI (2012) Entangled granular media. *Phys. Rev. Lett.* 108(20):208001.
18. Gabbriellini R, Jiao Y, Torquato S (2014) Dense periodic packings of tori. *Phys. Rev. E* 89:022133.
19. Jaeger HM (2015) Toward jamming by design. *Soft Matter* 11(1):12.
20. Ashton DJ, Jack RL, Wilding NB (2015) Porous liquid phases for indented colloids with depletion interactions. *Phys. Rev. Lett.* 114:237801.
21. Ungphaisoon S et al. (2010) Materials for microencapsulation: what toroidal particles ("doughnuts") can do better than spherical beads. *Soft Matter* 6(17):4070.
22. Lu X et al. (2007) Fabrication of cubic nanocages and nanoframes by dealloying Au/Ag alloy nanoboxes with an aqueous etchant based on $\text{Fe}(\text{NO}_3)_3$ or NH_4OH . *Nano Letters* 7(6):1764.
23. Au L et al. (2008) Synthesis and optical properties of cubic gold nanoframes. *Nano Res.* 1:441.
24. Chen C et al. (2014) Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces. *Science* 343(6177):1339.
25. Höger S (2004) Shape-persistent macrocycles: from molecules to materials. *Chem. Eur. J.* 10(6):1320.
26. Rothmund PWK (2006) Folding DNA to create nanoscale shapes and patterns. *Nature* 440(7082):297.
27. Veerman JAC, Frenkel D (1992) Phase behavior of disklike hard-core mesogens. *Phys. Rev. A* 45(8):5632.
28. van der Kooij FM, Kassapidou K, Lekkerkerker HNW (2000) Liquid crystal phase transitions in suspensions of polydisperse plate-like particles. *Nature* 406(6798):868.
29. Patti A, El Masri D, van Roij R, Dijkstra M (2009) Stringlike clusters and cooperative interlayer permeation in smectic liquid crystals formed by colloidal rods. *Phys. Rev. Lett.* 103:248304.
30. Donev A et al. (2004) Improving the density of jammed disordered packings using ellipsoids. *Science* 303(5660):990.
31. Jiao Y, Torquato S (2011) Maximally random jammed packings of platonic solids: hyperuniform long-range correlations and isotaticity. *Phys. Rev. E* 84:041309.
32. McGrother SC, Williamson DC, Jackson G (1996) A re-examination of the phase diagram of hard spherocylinders. *J. Chem. Phys.* 104:6755.
33. Bolhuis P, Frenkel D (1997) Tracing the phase boundaries of hard spherocylinders. *J. Chem. Phys.* 106(2):666.
34. Wu L, Wensink HH, Jackson G, Müller EA (2012) A generic equation of state for liquid crystalline phases of hard-oblate particles. *Mol. Phys.* 110(11-12):1269.
35. Giri N et al. (2015) Liquids with permanent porosity. *Nature* 527(7577):216.
36. Weeks JD, Chandler D, Andersen HC (1971) Role of repulsive forces in determining equilibrium structure of simple liquids. *J. Chem. Phys.* 54(12):5237.
37. Jover J, Haslam A, Galindo A, Jackson G, Müller E (2012) Pseudo hard-sphere potential for use in continuous molecular-dynamics simulation of spherical and chain molecules. *J. Chem. Phys.* 137(14):144505.
38. Gao J, Weiner JH (1989) Contribution of covalent bond force to pressure in polymer melts. *J. Chem. Phys.* 91(5):3168.
39. Hoover WG (1985) Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* 31(3):1695.
40. Melchionna S, Ciccotti G, Holian BL (1993) Hoover NPT dynamics for systems varying in shape and size. *Mol. Phys.* 78(3):533.
41. Smith W (2006) DL_Poly-applications to molecular simulation II. *Mol. Simul.* 32(12-13):933.
42. Schilling T, Pronk S, Mulder B, Frenkel D (2005) Monte carlo study of hard pentagons. *Phys. Rev. E* 71:036138.
43. Torquato S, Zhang G, Stillinger FH (2015) Ensemble theory for stealthy hyperuniform disordered ground states. *Phys. Rev. X* 5:021020.