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PAPER

Phase behavior of rounded hard-squares†

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Recently, Zhao *et al.* [*Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 2684] reported the phase behavior of monolayers of polymeric Brownian squares platelets. As the density is increased, this system exhibits the formation of two crystal structures not expected for particles with square symmetry, namely, a hexagonal rotator crystal phase and a rhombic crystal phase. Molecular simulations by Wojciechowski and Frenkel [*Comp. Met. Sci. Technol.*, 2004 **10**, 235] had predicted instead the formation of tetratic and square crystal phases. In this work, we report Monte Carlo simulation results of rounded hard squares of varying degrees of roundness, hence interpolating between disks and perfect squares. Our simulations show that the roundness of the particles gives rise to the phases observed by Zhao *et al.* and further provide a roadmap for the regions of stability of different ordered phases as a function of particle roundness. In particular, our results suggest that depending on the degree of roundness, the isotropic phase would transition either into a hexagonal rotator phase through a hexatic-like intermediate, into a square phase through a tetratic-like intermediate, or (in a narrow range of crossover values of roundness) into a novel polycrystalline phase containing domains with square order in coexistence with clusters of particles having a weak hexagonal order.

1 Introduction

At sufficiently high densities, systems composed of particles interacting *via* purely repulsive potentials can assemble into ordered phases driven by purely entropic forces. Colloidal particles under confinement in the form of monolayers or films are important not only for practical applications, but also from a theoretical viewpoint since their behavior in such a quasi two-dimensional situation is still not completely understood. The melting of hard discs (HD) in two dimensions (2D),¹ for example, has been actively studied to establish whether or not it follows a Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) mechanism, where the melting would happen through two continuous phase transitions.^{2–4} In the KTHNY theory, the 2D solid should melt first into a hexatic phase characterized by short range translational order and quasi-long range bond orientational order.⁵ The recent simulation results reported by Bernard and Krauth⁶ suggest that the melting does occur in two steps, as predicted by the KTHNY, but one of the steps involves a first order liquid–hexatic phase transition.

Anisotropic hard-particles can exhibit a richer phase behavior than isotropic particles as a result of the competition between translational and orientational entropic contributions.⁷ Molecular simulations of long hard-spherocylinders (cylinders of

length L and height σ capped at each end by two hemispheres of diameter σ) confined to lie on a plane showed that this system forms a nematic phase at high densities *via* a continuous isotropic–nematic transition.⁸ More recently, the phase behavior of hard-pentagons and hard-squares in 2D have also been studied *via* molecular simulations. The compression of hard-pentagons was found to lead first to the formation of a hexagonal rotator crystal (RHX) phase, followed by the formation of a striped phase, in which the centers of the particles are placed in a non-equilateral hexagonal lattice structure.⁹ The latter phase is observed as a result of a geometrical frustration of the pentagons; *i.e.*, it is impossible to have a periodic crystal with five-fold symmetry.¹⁰ On the other hand, hard-squares at high densities show the formation of a square solid (SX) phase, which is the expected space-filling lattice for this symmetry.¹¹ Interestingly, the formation of the square phase, as in the HD model, follows a two-step scenario in which by compressing the liquid phase the system exhibits first the formation of a tetratic (T) phase characterized by quasi-long range four-fold orientational order and short-range translational order. The T phase has also been observed in the simulation of hard rectangles (domino-shaped) particles.¹²

Experimental systems of Brownian colloidal particles with square and pentagon shapes have also been reported in the literature.^{13,14} As predicted by simulation,⁹ Brownian pentagons exhibit the formation of the RHX phase¹³ in 2D. However, at high densities the RHX transforms into a frustrated rotator crystal, instead of the stripe-like phase observed in simulations. A similar trend is also observed in squares particles, where the

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system does not self-assemble into the T and SX phases predicted by the simulations, but forms instead the RHX and rhombic (RB) crystal phases. Zhao *et al.*¹⁴ conjectured that this discrepancy could be due to a combination of such factors as the particle roundness in experiments and potential artifacts in the simulations (like the imposition of square boxes). In this article, we show that by changing the extent of corner rounding in the squares, different types of ordered phases can be accessed, including those observed in the experiments.

2 Model

We adopted a simple model of a 2D rounded-corner hard-square (RCHS) system where each particle is constructed by piecing together four two-dimensional hard-spherocylinders of aspect ratio $L^* = L/\sigma$ (see Fig. 1), representing the four edges of the square particle (the internal hole in this model is irrelevant for 2D simulations). Either the aspect ratio L^* or the corner-rounding-to-length ratio $\zeta = \sigma/(L + \sigma) = (1 + L^*)^{-1}$ is used to characterize the roundness of the particles. This model is suitable to interpolate continuously between the HD system for $\zeta \rightarrow 1$ (or $L^* \rightarrow 0$) and the hard-square system in the limit $\zeta \rightarrow 0$ ($L^* \rightarrow \infty$). As the roundness of the system is varied, the system exhibits the formation of different phases, and for an appropriate choice of ζ , it can approximate the experimental behavior of Brownian squares.¹⁴

Monte Carlo (MC) simulations were performed in the isothermal-isobaric NPT ensemble with standard periodic boundary conditions. Since a rectangular box might induce the formation of artificial phases, the isothermal-isostress $N\sigma_P T$ ensemble was also used at high densities as it allows triclinic changes in the shape of the box.¹⁵ The formation of ordered phases is detected using several global order parameters. The bond order parameters Ψ_4 and Ψ_6 are used to detect four-fold and six-fold bond angular order, respectively. These parameters are defined as: $\Psi_n = (1/N) |\sum_{j=1}^N (1/n_j) \sum_{k=1}^{n_j} \exp(in\theta_{jk})|$, for $n = 4$, and 6, respectively. In this equation, N is the total number of particles, θ_{jk} is the angle made by the bond between particle j and its nearest neighbor with respect to an arbitrary axis, and n_j is the number of nearest neighbors of particle j . For Ψ_6 , n_j is calculated using the Voronoi tessellation,¹⁶ while for Ψ_4 the four closest neighbors of each particle are used. The global orientational order of the molecular axis is analyzed using the parameter Φ_4 , defined as $\Phi_4 = (1/N) |\sum_{j=1}^N \exp[i4(\theta_j \bmod (2\pi/4))]|$, where θ_j is the angle between one of the molecular axes of square j and an arbitrary reference fixed axis (the modulus function is used to account for the four-fold symmetry of the squares). The spatial range of orientational order was quantified using the orientational distribution function $g_{4\phi}(|\mathbf{r}|) = \langle \phi_4^*(\mathbf{r}') \phi_4(\mathbf{r}) \rangle$, where $\phi_4(\mathbf{r})$ is the local orientational order parameter evaluated at distance $\mathbf{r}$. Translational order in the system is obtained by using the global translational order parameter defined as $\psi_T = (1/N) \sum_{j=1}^N \exp(i\mathbf{G} \cdot \mathbf{r}_j)$, where $\mathbf{G}$ is a reciprocal lattice vector for the appropriate crystal structure. Translational order can also be detected analyzing the behavior of the radial distribution function $g(|\mathbf{r}|)$ and the six-fold bond orientational correlation function $g_k(|\mathbf{r}|) = \langle \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r}) \rangle$ (where $\psi_k(\mathbf{r})$ is the k -fold local bond orientational order at position $\mathbf{r}$).

The regions of stability of the phases encountered for a given system were found by mapping out the equation of state (EoS) *via* compression and expansion runs. The compression runs were started using a low density isotropic state with random positions and orientations of the particles. The expansion runs were started with perfect crystal structures obtained using the method reported by Filion *et al.*¹⁷ To detect the points where phase transitions occur, we looked for not only breaks and inflection points in the EoS curves, but also for spots where fluctuations of the bond order parameters (susceptibilities), defined as $\chi_n = N(\langle \Psi_n^2 \rangle - \langle \Psi_n \rangle^2)$, diverge or have large peaks.¹⁸ The latter method has been found to be less sensitive to finite size effects than the former.¹⁹ Since the EoS and transition points found by compression and expansion runs exhibited little hysteresis and we are only interested in approximate boundaries, there was not need to perform complementary (and costly) free energy calculations.

We introduce conventional reduced units to describe the different thermodynamic states and structural properties. Accordingly, the reduced pressure and packing fraction are defined as $P^* = P\sigma^2/(k_B T)$ and $\eta = NA_p/A$, where P is the pressure, k_B is Boltzmann's constant, T is the absolute temperature, A is the total area of the system, and $A_p = [(L + \sigma)^2 - (1 - \pi/4)\sigma^2]$ is the particle area of the RCHS, respectively.

3 Results

As validation of the model, the $\zeta = 0.01$ RCHS system was studied as it essentially corresponds to perfect hard squares. The equation of state (EoS) for such a case was found to be in good agreement with the molecular simulation results reported in ref. 11 (see supplemental material†²⁰).

As a next step, we determined an approximate phase diagram of the RCHS system as a function of ζ by using a small system ($N = 400$ particles). This system size is likely too small to conclusively determine the nature and the location of the phase transitions; however, it allows a fast determination of the different phases exhibited by the system by mapping out the EoS of a given system *via* expansion and compression runs. Note that simulations of bigger systems (from $N = 1600$ to 4096 particles) were also performed in selected cases and found to give consistent results (as described later).

The approximate phase diagram of RCHS as a function of ζ obtained from compression runs is shown in Fig. 1. The EoS for each system can be found in the supplemental material†. As can be observed in Fig. 1, the model reproduces well the two limits, namely, HD and hard-squares, respectively. The $\zeta = 0.8$ RCHS system exhibits a similar behavior as the HD, in that the isotropic (I) and RHX phases are observed. This shows that the curvature of the $\zeta = 0.8$ system is still large enough to preserve the hexagonal symmetry observed in HD for the range of densities considered in this work. A different situation is observed when the curvature is decreased. The $\zeta = 0.667$ RCHS system forms, as in the previous case, the I and RHX phases, but at high densities it now forms the RB phase. The molecular simulation study of the closed-packed structures of convex superdiscs reported by Jiao *et al.*²¹ revealed the formation of a similar structure as the RB phase, which they called Δ_1 lattice.

Fig. 1 (Top panel) Description of the model used to model the RCHS particles. (Bottom panel) Equation of state for 400 RCHS particles in the $\eta - \zeta$ (or equivalent $\eta - L^*$) plane calculated from Monte Carlo simulation from compression runs. The phase boundaries for the $\zeta = 1$ limit corresponding to the hard disk model are taken from ref. 24 (the hexatic boundaries are not shown in the diagram as they strongly depend on the system size). The upper limit for $\zeta = 1$ corresponds to the close packing fraction of HD. The isotropic (I) phase is denoted by circles ($\circ$), the hexagonal rotator crystal phase by up-triangles (Δ), the rhombic crystal phase by diamonds ($\diamond$), square crystal phase by squares ($\square$), and the polycrystalline phase by filled right-triangles ($\blacktriangleright$). The (blue) rectangle marks the approximate region where the tetratic phase is located according to our large-system simulations (and ref. 11 for perfect squares).

As the value of ζ is increased, the range of densities at which the RHX phase is stable is reduced, while that of the RB phase is increased. In fact, the maximum value of ζ at which the RHX phase is expected to vanish can be estimated using the phase diagram of the HD system and some geometrical arguments as follows. Recall first that the densest packing of HD is $\eta_{\text{HD}}^{\text{CP}} = \pi/\sqrt{12}$. In the RHX phase, the particles are positioned in a regular triangular lattice, rotating freely along their centers of mass and sweeping an effective circular area of $A_{\text{eff}} = (\pi/4)D^2$, where $D = (\sqrt{2}L + \sigma)$ is the diagonal of the particles (*i.e.*, the diameter of the circle circumscribing each of the particles). Hence, the maximum packing fraction of hexagonal order of equivalent freely rotating RCHS is given by $\eta_{\text{RCHS}}^{\text{RHX}} = \eta_{\text{HD}}^{\text{CP}}(A_p/A_{\text{eff}})$. It is evident that as ζ decreases the value of $\eta_{\text{RCHS}}^{\text{RHX}}$ also decreases. At the point where $\eta_{\text{RCHS}}^{\text{RHX}}$ reaches the same value as the densest isotropic state observed in the simulation (for the corresponding ζ system) the RHX would no longer be stable. This point corresponds to the system with $\zeta \approx 0.444$, in which $\eta_{\text{RCHS}}^{\text{RHX}}$ takes on the value of 0.715, while the packing fraction of the densest isotropic state for the same system is 0.733. The actual phase diagram shows that the RHX persists in a small region for $0.444 \geq \zeta \geq 0.4$; this discrepancy can be explained by the fact that the RHX phase observed for $\zeta \leq 0.444$ has a significantly less perfect hexagonal order than that for $\zeta > 0.444$. In fact, for $\zeta \leq 0.444$ one observes that the values of Ψ_6 are lower while the values for Ψ_4 and Φ_4 are no longer negligible.²⁰

For low values of ζ ($\zeta < 0.333$) there is no indication of the formation of an RHX phase for the range of pressure studied in this work (at higher pressures these systems might still exhibit the formation of an RB phase, except for the case of perfect squares). The stability of the RB phase with respect to the RHX phase for the RCHS system has already been rationalized by Zhao *et al.*¹⁴ using a mean field model entailing similar geometrical arguments.

Around $\zeta = 0.333$, RCHS exhibits a very interesting crossover phase behavior between disk-like and square-like behavior; this is described in detail at the end of this section.

The stable phases observed in simulation for the systems with large values of ζ ($0.667 \geq \zeta \geq 0.333$) agree well with the experimental results reported by Zhao *et al.*¹⁴ However, the roundness of their synthesized square particles is reported to be approximately $\zeta_{\text{exp}} \approx 0.25$. This difference might be due to several reasons. One possible cause is the true dimensionality of the experimental system. Zhao *et al.* produced a monolayer of square particles on the bottom of an optical cuvette with the aid of roughness-controlled depletion attraction²² between the flat surface of the particles and the glass bottom wall. While presumed negligible effects, our 2D model does not account for any substrate-particle or particle-particle lateral interactions, nor for the finite height and roughness of the particles. It is important to note that in the experimental system the packing fractions at which the RHX and RB phases occur are significantly lower than those in our simulations. If one rules out any role of metastability on such observations, there is no obvious culprit that may explain such discrepancies, though experimental uncertainties on such measurements as particle area and finite size effects in the simulations could be small contributors. We also recomputed the EoS for the $\zeta = 0.308$ RCHS system using compression runs but only allowing particle rotation of less than 5° to preclude “tip crossing” events which do not happen in the experimental systems (and could have favored metastable structures). We found that neither the stable phases nor the phase boundaries were affected by such small rotations, indicating that the discrepancy between our model and the experimental system is not due to tip-crossing effects. Notwithstanding these differences, our results show that *actual* particle roundness (augmented by any underlying experimental effect that may increase the *apparent* particle roundness) is a key element in explaining the phase behavior of the experimental system.

As mentioned before, the system with the largest value of ζ studied in this work that exhibits the formation of the RB phase corresponds to $\zeta = 0.667$. To obtain a deeper understanding of this case, we have performed simulations using a larger system with $N = 1600$ particles. The results are shown in Fig. 2 including the equation of state data for the $N = 400$ particle system for comparison. The EoS for the small and large systems from compression runs agree well over the entire range of densities, with only small differences observed at high pressures due to the presence of defects in the RB phase. A similar trend has been observed for the expansion runs of the same system.²⁰ At low densities, all the order parameters have values close to zero, which is characteristic of the I phase. By compressing the system up to $\eta \approx 0.71$, the bond-order parameter Ψ_6 increases significantly while the parameters Ψ_4 and Φ_4 remain close to zero. This

Fig. 2 Equation of state for 1600 RCHS particles with $\zeta = 0.667$ obtained by expansion runs. (Top panel) The pressure P^* , bond orientational order parameters Ψ_4 and Ψ_6 , orientational order parameter Φ_4 , and hexagonal translational order parameter $\psi_{T, \text{hex}}$ as a function of the packing fraction η . For comparison, the equation of state curve obtained for the system of $N = 400$ particles is also shown (continuous curve). (Bottom panel) Cross order parameters $\Psi_4\Phi_4$ and $\Psi_6\Phi_4$, and susceptibilities of the bond order parameters χ_4 and χ_6 as a function of η .

is characteristic of an RHX, in which the particles are arranged in a triangular lattice, each having six nearest neighbors, with the vectors characterizing the molecular orientations pointing at different directions. This behavior can also be readily detected by analysing the cross parameter $\Psi_6\Phi_4$ also shown in Fig. 2; this parameter is negligible for $\eta < 0.84$, which indicates that there is no coupling between the particle orientation and the (six) neighbor positions. In the region where the I–RHX phase transition is observed, discontinuities in the values for the packing

Fig. 3 (Left) Definition of the lattice angles α_1 and α_2 used to characterize the crystal structures. (Top panel) The lattice angles for the RHX phase are calculated using the nearest neighbors of the central particles (blue light particles), which have been determined using the Voronoi tessellation. (Bottom panel) The lattice angles for the SX phase are calculated with the vectors $\vec{u}$ and $\vec{v}$ (denoted with red arrows) obtained using only the coordinates of the four nearest neighbors of the central particles (blue light particles). The lattice angles for the RB phase can be calculated using either method. (Right) Lattice angles as a function of the packing fraction η for (a) RCHS with $\zeta = 0.667$, and (b) RCHS with $\zeta = 0.286$.

fraction and in the bond order parameter Ψ_6 would indicate that the I–RHX transition is first order. However, the results obtained with different system sizes ($N = 400$, 1600, and 4096 particles) differ in the location of the transition point, suggesting that the system sizes studied in this work are still too small to resolve the nature of the transition. However, the agreement of the results away from this region confirms the correct determination of the different phases obtained for this system. Note that finite size effects in this region have also been observed in the expansion runs. By further increasing the density of the system, the RB phase is observed where particle orientations spontaneously align as indicated by the large values of Φ_4 ; the non-zero values of Ψ_6 and the large values of Ψ_4 are further indicators of the RB phase. In Fig. 4 two representative snapshots of the RHX and RB phases for this system are presented, including the corresponding structure factors obtained from

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \left[\sum_{i=1}^N \cos(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 - \left[\sum_{i=1}^N \sin(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 \right\rangle.$$

The transformation between the RHX and RB phases can also be observed by calculating the lattice angles of the crystal structures. For the RHX phase the lattice angle should be close to $\alpha_1 \approx 60^\circ$, while for the RB the lattice angle is expected to be $\alpha_1 > 60^\circ$. Such a change in the lattice angle is clearly observed in Fig. 3(a) as the system moves from the RHX phase to the RB phase with increasing density. In the RB region, the limiting value of the lattice vector is $\alpha_1 \approx 66.9^\circ$, which is close to the value of the lattice angle calculated from the determination of the crystal structures using the method of Filion *et al.*,¹⁷ i.e., $\alpha_1 \approx 67.8^\circ$ (see ref. 20). As in the case of the I–RHX transition, the results close to the RHX–RB transition exhibit some small discrepancies for simulations using $N = 400$, 1600, and 4096 particles. For the simulations using $N = 400$ and $N = 1600$ particles the EoS shows a cusp in the transition which might indicate either a weak first order or second order phase transition. However, for the system $N = 4096$ the cusp disappears, suggesting that the transition is second order. The latter result is inconsistent with the observations of Zhao *et al.*,¹⁴ suggestive of a first order nature for the RHX–RB transition in Brownian squares.

To gain some insights on the nature of the transition between the I and RHX phases, we carried out MC simulations in the canonical NVT ensemble for a system of 5625 particles in a square box for different densities. Fig. 5 shows the radial

Fig. 4 Representative snapshots and corresponding structure factors for a system of $N = 1600$ RCHS with $\zeta = 0.667$ obtained by compression runs. (left) RHX phase ($P^* = 16.0$), and (right) RB phase ($P^* = 50.0$).

Fig. 5 Correlation functions for the systems of $N = 5625$ RCHS with $\zeta = 0.667$ obtained from MC-NVT simulations. The radial $g(r)$ and bond-order $g_6(r)$ correlation functions are shown for three different packing fractions corresponding to $\eta = 0.708$, $\eta = 0.710$, and $\eta = 0.712$. The dashed-line with slope $1/4$ corresponds to the algebraic decaying of the correlations in the hexatic-solid transition predicted by the KTHNY theory. The snapshot and the corresponding structure factor of the system with $\eta = 0.710$ are presented in the bottom frame.

distribution function $g(|\mathbf{r}|)$ and the bond orientational correlation function $g_6(|\mathbf{r}|)$ for three different densities close to the I–RHX phase transition (see Fig. 2). As can be observed from the behavior of $g(|\mathbf{r}|)$, these systems show no translational order, but in all cases the correlation function $g_6(|\mathbf{r}|)$ decays algebraically, *i.e.* $g_6(|\mathbf{r}|) \sim r^{-\eta_\phi}$ with $\eta_\phi = 0.18$ and 0.1 for $\eta = 0.710$ and 0.712 , respectively. Fig. 5 also shows the structure factor for $\eta = 0.710$ which displays patterns of concentric hexagons typical of hexatic order. The behavior of these hexatic-like phases seems to suggest that the I–RHX transition involves a two-step mechanism, similar to the one observed for the HD system. However, simulations employing much larger systems would be required to obtain more conclusive details.

As indicated before, RCHS systems with $\zeta < 0.333$ no longer form the RHX phase, forming the T and SX phase instead. In order to analyze this situation more accurately, we have simulated the phase behavior for a system of 4096 RCHS with $\zeta = 0.286$, which is shown in Fig. 6. As in the previous case, we also include the EoS for the system of $N = 400$ particles for

Fig. 6 Phase diagram for 4096 RCHS with $\zeta = 0.286$ obtained by expansion runs. Legend as in Fig. 2.

comparison. As can be observed in Fig. 6, the EoS obtained from the small and large systems agree very well and reveal three phase transitions. The first one, observed at $\eta \approx 0.76$, is the transformation from an I phase into a T phase characterized by the values of Ψ_4 and Φ_4 approximately in the range 0.4 – 0.8 . The properties of the T phase can be analyzed using the structure factor $S(\mathbf{k})$, the radial distribution function $g(|\mathbf{r}|)$, the bond orientational correlation function $g_4(|\mathbf{r}|)$, and the orientational distribution function $g_{4\phi}(|\mathbf{r}|)$ (see Fig. 7). In $S(\mathbf{k})$ the formation of diffuse peaks with four-fold symmetry can be observed, which is consistent with tetratic-like behavior.¹² For this phase, $g(|\mathbf{r}|)$ shows liquid-like behavior, while the

Fig. 7 Correlation functions for the systems of $N = 4096$ RCHS with $\zeta = 0.286$ obtained from MC-NPT simulations. (Left) The radial $g(r)$, bond-order $g_4(r)$, and orientational $g_{4\phi}(r)$ correlation functions for three different pressures corresponding to $P^* = 12.5$ (T phase), $P^* = 18.0$ (SX phase), and $P^* = 50.0$ (RB phase) are shown. (Right) The snapshot and the corresponding structure factor for (top) $P^* = 50.0$, (middle) $P^* = 18.0$, and (bottom) $P^* = 12.5$ are also shown.

distribution functions $g_4(|\mathbf{r}|)$ and $g_{4\phi}(|\mathbf{r}|)$ decay algebraically. This behavior indicates that this phase possesses short range translational order while still having quasi-long ranged orientational order.^{11,12} The second transition, observed at $\eta \approx 0.825$, is the transformation of the T phase into the SX phase. As in the case of the T phase, the SX phase can be identified using the different distribution functions and the structure factor. The structure factor shows sharp peaks with square symmetry, which is in line with the long range behavior observed in the distribution functions $g_4(|\mathbf{r}|)$ and $g_{4\phi}(|\mathbf{r}|)$, and the quasi-long ranged behavior detected in $g(|\mathbf{r}|)$. As expected, for this phase Ψ_6 remains close to zero, while Ψ_4 and Φ_4 keep increasing as a consequence of the enhancement of the square order. The third and last transition observed for this system occurs at $\eta \approx 0.87$, which involves the transformation of the SX phase into a RB phase. This transition is more difficult to analyze using the different distribution function as they show similar behavior in both SX and RB structures. This transition, however, can be more easily detected by calculating the distribution of the lattice angles in the crystal structures. It is expected that for the SX (and T) phase the angle distribution will exhibit the formation of a single peak centered at $\alpha_1 = \alpha_2 = 90^\circ$, while for the RB phase peaks at two angles should be observed (one $< 90^\circ$ and the other $> 90^\circ$, adding up to 180°). Again, from the calculation of the crystal structures using the method by Filion *et al.*,¹⁷ the lattice angle for the RB phase in this system should approach the limit value of $\alpha_1 \approx 80.435^\circ$. The results for the lattice vector for this system as a function of the packing fraction are shown in Fig. 3(b), where the point where the phase transition takes place is clearly seen. Returning to Fig. 6, it can be seen that for the RB phase the already high values of Ψ_4 and Φ_4 keep increasing with density, while Ψ_6 increases from a low value to a non-zero finite value due to the formation of the oblique lattice in the RB phase. While one could have expected that Ψ_4 in the RB phase would be smaller than that for the SX phase, the opposite is observed in Fig. 6. This can be explained by analyzing the snapshots of typical configurations and the distribution of the lattice angles. The snapshots (see Fig. 7) reveal that, unlike the situation in the RB phase, the particles in the SX phase still have enough free space to rotate along their lattice positions (and give a lower value of Ψ_4). This difference in orientational freedom is consistent with the angle lattice distributions (results not shown) that show two narrow peaks for the RB phase, while a broad peak centered at $\alpha_1 = 90^\circ$ for the SX phase. For this system, the phase behavior obtained by compression and expansion runs agree very well, as do the results for different system sizes ($N = 400$, 1600 and 4096 particles), which indicates that finite size effects are less significant in this case.

Finally, we focus on the behavior of RCHS for values of ζ in the vicinity of the crossover between disk-like and square-like behaviors. Analyzing Fig. 1 it seems that such a crossover takes place near $\zeta \approx 0.333$. Upon compression of this system, the isotropic phase transitions at $\eta = 0.76$ into a phase having both hexagonal-like and square-like structural motifs (see Fig. 8). At the transition point the susceptibilities of both bond order parameters χ_4 and χ_6 increase to roughly the same value. This is suggestive of a situation where the particles have comparable proclivity to form either RHX or SX/RB type of structures.

Fig. 8 Phase diagram for 4096 RCHS with $\zeta = 0.333$ obtained by expansion runs. Legend as in Fig. 2.

This structural competition seems to lead to the formation of a polycrystalline phase where clusters of particles forming an SX/RB phase coexist with clusters of particles having a weak hexagonal packing. This polycrystalline phase is also observed in the expansion runs and in small and large system sizes. Fig. 9 shows the results for the structure factor and the corresponding configuration of the system at $P^* = 12.5$. In the structure factor, peaks corresponding to tetragonal-like, RHX-like and RB-like behavior are observed, confirming the heterogeneous nature of the micro-domains. The top and bottom frames in Fig. 9 (showing the same snapshot for two coloring schemes)

Fig. 9 Snapshot of the polycrystalline phase for the system of $N = 4096$ RCHS with $\zeta = 0.333$ obtained from MC-NPT simulations at $P^* = 12.5$. The corresponding structure factor is also shown. (Top panel) Particles are colored with respect to the average distance between a central particle and the four nearest neighbors (in units of the diagonal of the particles, which for this specific system takes the value of $D/\sigma = 3.828$). (Bottom panel) Particles are colored with respect to the local value of Ψ_4 .

demonstrate that there is a correlation between regions of higher density and regions of higher square-order. To rule out the possibility that either this state lies in a two phase region and we are observing a metastable state with incomplete macrophase separation, or that the system unduly trapped too many defects, we performed several simulations in the *NVT* ensemble with $N = 12288$ particles using as an initial state a configuration consisting of two phases (in an elongated box) separated by a straight interface. One of these phases was an equilibrated RB phase obtained from the *NPT* simulations of the same system, while the other phase consisted of an I phase close to the density at the transition point. The overall density of the systems studied was always in the $0.76 < \eta < 0.80$ region where the polycrystalline domains were observed during the *NPT* simulation. In all cases and regardless of the initial conditions chosen, the interface between the two phases rapidly vanished and the system always ended up forming the same polycrystalline phase. The formation of this polycrystalline phase can be seen as a good example of shape-induced frustration in a colloidal system,²³ wherein even small symmetry-conserving changes in the shape of the particles can induce the formation of a new unusual phase. At approximately $\eta \approx 0.80$, the polycrystalline phase transforms into the RB phase, without a T or SX intermediate phase.

4 Conclusions

We have shown in this work that the corner curvature of square particles has an important effect in their 2D phase behavior, as speculated in ref. 14. Systems with large curvature show more of a HD-like behavior, where a RHX phase is observed first, followed by a RB phase formed by the alignment of the particle orientations at high densities. On the other hand, particles with low curvature show a square-like behavior, with the formation of a SX phase first, followed by a RB phase. The crossover between such HD-like and square-like phase behaviors occurs at around $\zeta \approx 0.333$, where our large-system simulations reveal the formation of a new polycrystalline phase having small rhombic crystallites surrounded by regions of more loosely hexagonally packed particles. Further studies, however, would be needed not only to clarify the thermodynamic nature of the different order-disorder transitions observed (*e.g.*, using much larger systems) but also to measure their kinetics and the dynamic properties of the hexatic-like, tetratic-like, and polycrystalline phases. Such studies may also be helpful in elucidating the quantitative discrepancies observed between our results and the experimental data of Zhao *et al.*¹⁴

Note added after first publication

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