Supplemental Material to Nonconventional Phases of Colloidal Nanorods with a Soft Corona

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Isotherms of the equation of state of SS-SCs

The phase diagram of softened-square-shoulder spherocylinders (SS-SCs) with a length-to-diameter ratio $L/\sigma = 5$ and shoulder length $\lambda/\sigma = 1.35$, is constructed by mapping out isotherms of the equation of state (EOS). The smectic order parameter τ, and bond-orientational order parameters Ψ_n, with $n = 4$, 6 and 12, along with the $P^* - \rho^*$ EOS isotherms are presented in Figs. 1 and 2 for the range of reduced temperature $0.12 \leq T^* \leq 0.30$ and reduced pressure $0.05 \leq P^* \leq 10.0$.

In Fig. 3, the isotherm of the $P^* - \rho^*$ EOS of a system of $N = 1600$ SS-SCs with $L/\sigma = 10$ (effective $L/\lambda \sim 7.4$) at $T^* = 0.12$ is presented. Global smectic and nematic order parameters are included to highlight the region where the nematic (N) phase is stable. At this temperature, the range of packing fractions [8] where the N phase is found, matches the case of HSCs with $L/D = 7.4$. More specifically, in the HSCs with $L/D = 7.4$, the N phase approximately spans the range $0.34 < \eta < 0.45$ [1], whereas for the SS-SCs with $L/\lambda = 7.4$, the N phase appears to be stable in the range $0.30 < \eta < 0.46$.

In-layer structure of smectic phases

To characterize the in-layer structure of the equilibrium phases found in the studied parameter space, pair correlation functions perpendicular to the nematic director $g_{\perp,l}(r)$ are computed. The nematic director $\hat{\boldsymbol{n}}$ is the eigenvector associated to the largest eigenvalue (S) of the tensor

$$\boldsymbol{\mathcal{Q}}_{\alpha\beta} = \frac{1}{N}\sum_{i=1}^{N}\left[\frac{3}{2}\hat{\boldsymbol{e}}_{i\alpha}\hat{\boldsymbol{e}}_{j\beta} - \frac{\delta_{\alpha\beta}}{2}\right], \quad (1)$$

where $\hat{\boldsymbol{e}}_i$ is the orientation of particle i, $\alpha, \beta \in \{x, y, z\}$ and $\delta_{\alpha\beta}$ is the Kronecker delta. Geometrically, $\hat{\boldsymbol{n}}$ indicates the preferential orientation of the particles along the main particle axis.

Snapshots of equilibrium configurations of smectic liquid crystals with (SM) or without (SM*) overlap between particle coronas at $T^* = 0.12$ are shown in the left frame of Fig. 4. The difference in the in-layer structure can be appreciated by comparing their in-plane pair-correlation function $g_{\perp,l}(r)$, reported in the right frame of Fig. 4.

Formation of QC12 phases

In two-dimensional core-corona systems, the formation of a random-tiling high-density dodecagonal quasicrystal has been widely reported [2–6]. In these systems, such phase is generally obtained by compression of an isotropic phase to a high density at constant temperature or by cooling a hexagonal lattice from a high to a low temperature at constant density [2]. For the SS-SC system, we obtain states with smectic layers presenting in-layer dodecagonal symmetry (QC12 phase) by performing MC-NVT simulations where HDH crystals are cooled from a high to a low temperature ($T^* = 1.0$ to 0.12) keeping the quasi-2D density in the range of densities $0.92 < \rho^*_{\mathrm{2D,QC12}} < 0.95$. At these 2D densities, softened-square-shoulder disks, with similar potential parameters to those employed in our MC simulations, exhibit stable dodecagonal quasicrystals at temperatures $T^* < 0.3$.

To identify the formation of the QC12 phases, changes in the bond-orientational order parameters Ψ_n, with $n = 4$, 6 and 12, with temperature are tracked. In Fig. 5 we plot the average n-fold bond orientational order and reduced energy per particle $(U/N\epsilon)$ as a function of temperature for the MC-NVT cooling runs of SS-SCs at $\rho^* = 0.144$ ($\rho^*_{\mathrm{2D,QC12}} = 0.93$). At high temperatures, the dominant symmetry is hexagonal as $\Psi_6 > \Psi_{12} > \Psi_4$. The formation of the QC12 phase is clearly identified at $T^* = 0.20$, where $\Psi_{12} > \Psi_6 > \Psi_4$. To further test the stability of this phase, additional simulations are performed at the state points where we found the dodecagonal symmetry using a configuration consisting of smectic layers having the parallel aligned rods in dodecagonal motifs arranged in a triangle tiling (AC-tr approximant). As in the case of square-shoulder disks [7], we observe that the triangle tilling of the dodecagonal motifs is not retained, and instead, the formation of a random-tiling high-density dodecagonal quasicrystal, similar to that obtained from the cooling runs, occurs. In extensive simulations (consisting of up to 1.5×10^7 MC cycles) no further transitions to either HDH or SQ states are observed. Finally, in order to discard finite-size effects, the QC12 phase is also equilibrated by MC-NVT cooling simulations of a system of $N = 4160$ particles (4 stacked

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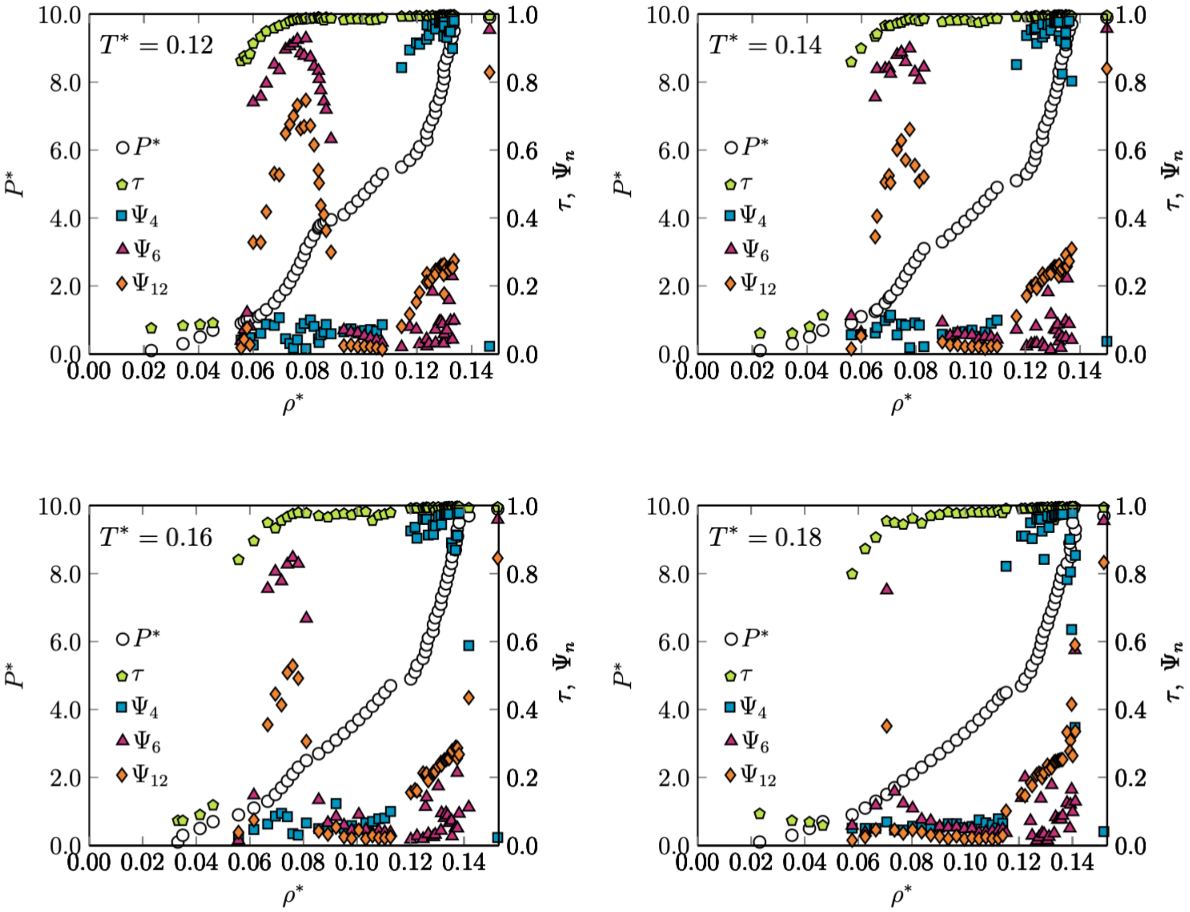

FIG. 1: Isotherms of the EOS $P^* - \rho^*$ of SS-SCs with a length-to-diameter ratio $L/\sigma = 5$ and shoulder length $\lambda/\sigma = 1.35$. The order parameters τ and Ψ_n (with n =4,6 and 12), characterizing the smectic order and in-plane symmetry, respectively, are included.

layers with 1040 particles per layer). In Fig. 6 we report a typical simulation snapshot and structure factor of the obtained QC12 phase at $\rho^* = 0.143$ and $T^* = 0.12$, showing that the 12-fold rotational symmetry is preserved in these larger systems.

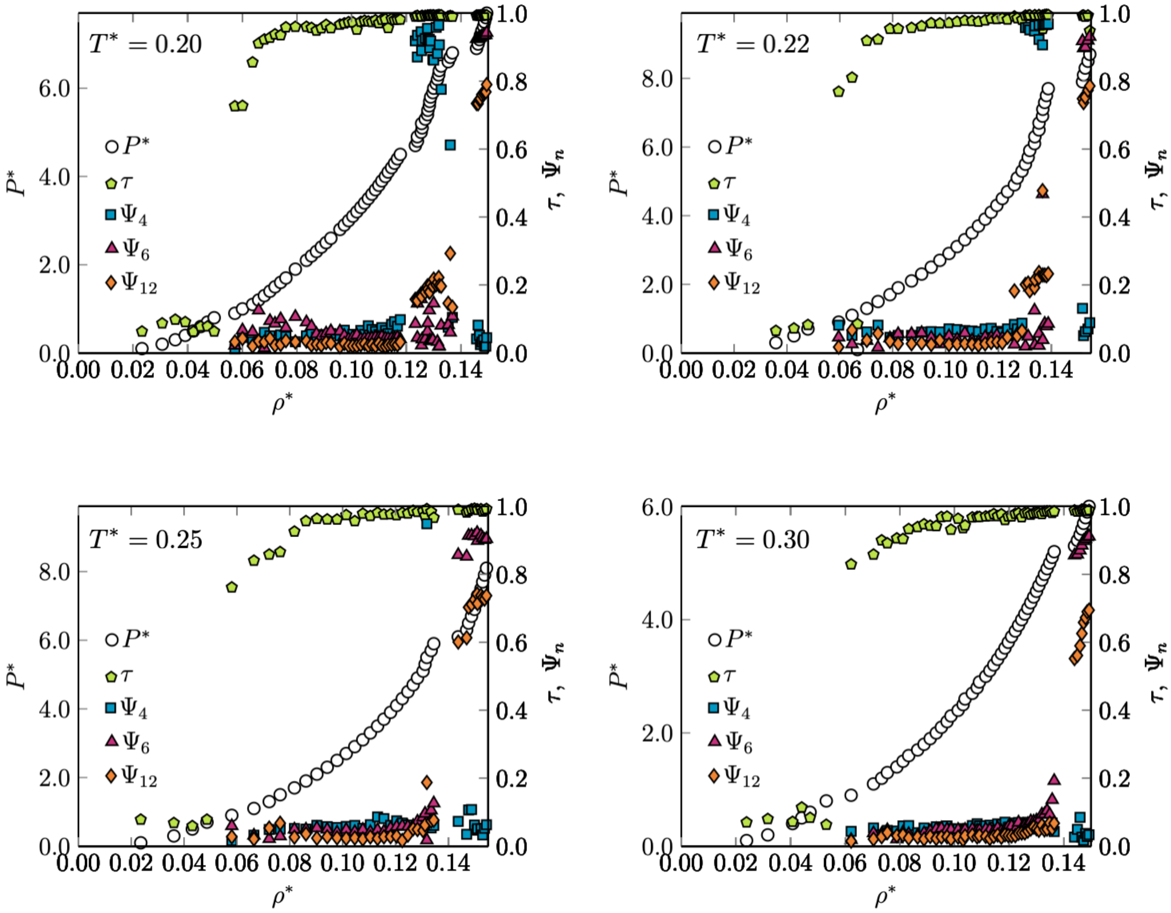

FIG. 2: Continuation of Fig. 1.

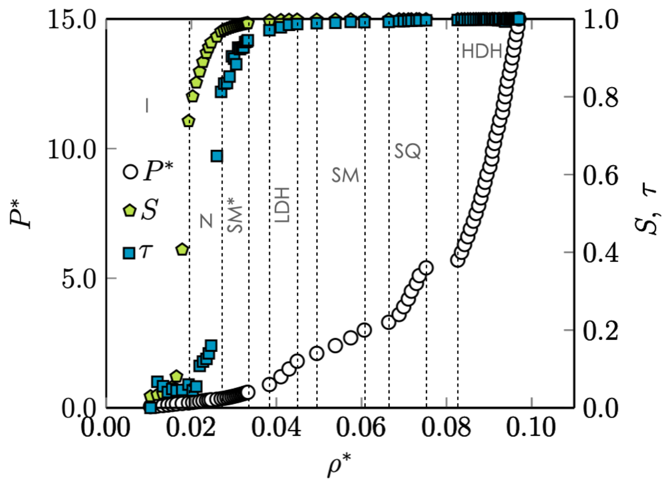

FIG. 3: Isotherm of the EOS of SS-SCs with a length-to-diameter ratio $L/\sigma = 10$ and shoulder width $\lambda/\sigma = 1.35$ at $T^* = 0.12$, obtained by expansion runs using $N = 1600$ particles. The global nematic (S) and smectic (τ) order parameters are included to identify the orientational and positional order in the simulated state points. Vertical dashed lines are added to differentiate the mechanically stable phases.

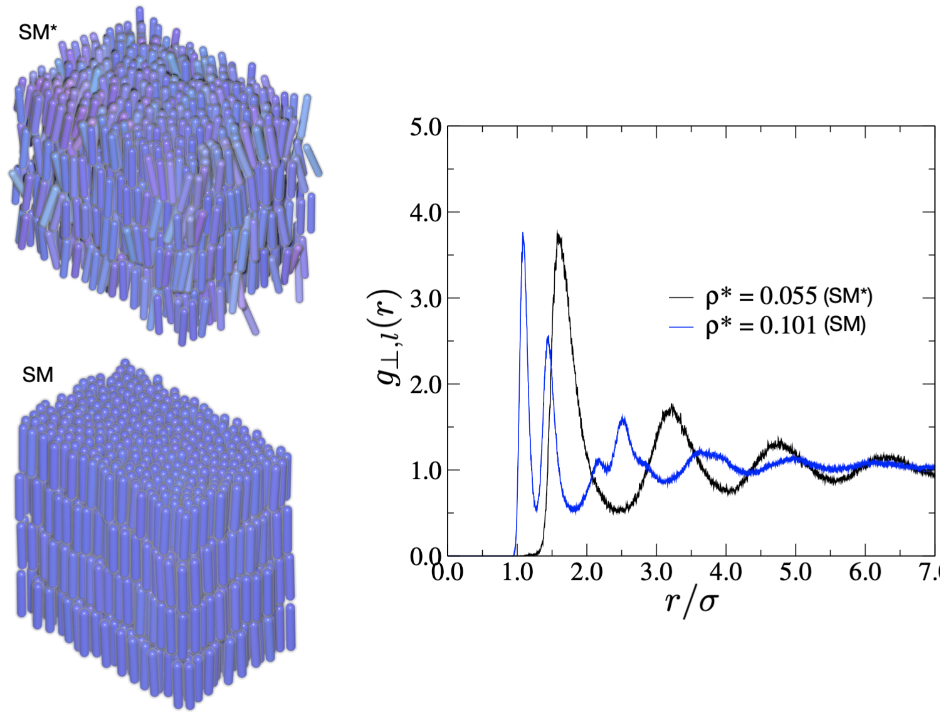

FIG. 4: Simulation snapshots (left) of equilibrated SM and SM* phases and their respective projection of the pair correlation function perpendicular to the director (right).

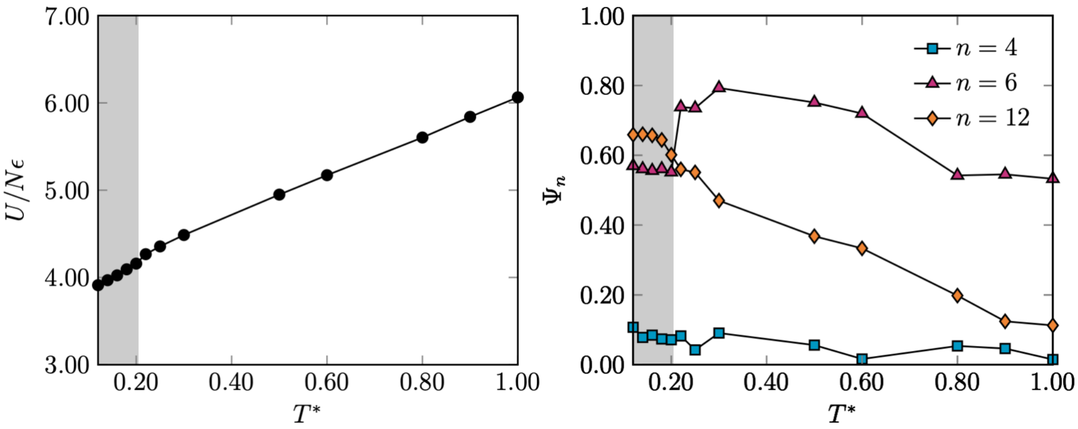

FIG. 5: Variation of the bond-orientational order parameters Ψ_n (with n =4,6 and 12) during the formation of the QC12 phase by temperature cooling of an HDH crystal at constant density $\rho^* = 0.144$. The shaded region indicates the range of temperatures where the in-layer dodecagonal symmetry becomes dominant with respect to the hexagonal and tetragonal symmetries.

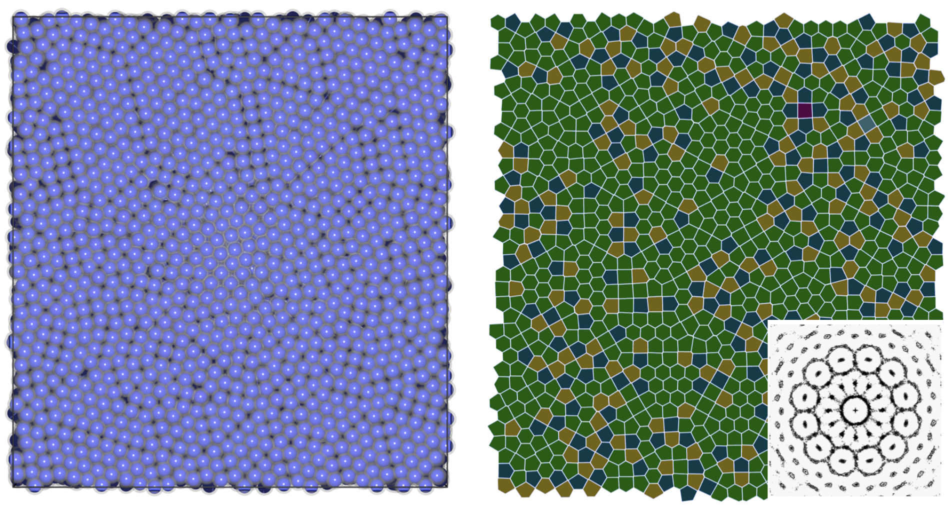

FIG. 6: Simulation snapshot of an equilibrated QC12 phase obtained by MC-NVT runs with $N = 4160$ particles (4 stacked layers with 1040 particles per layer) at $\rho^* = 0.143$ and $T^* = 0.12$ (left). The corresponding Voronoi diagram and structure factor, showing the in-plane order, are also included (right).

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[8] The packing fraction is defined as $\eta \equiv \rho \nu_{\mathrm{m}}$, where $\nu_{\mathrm{m}} = \pi(\lambda/2)^2\left[(4/3)(\lambda/2) + L\right]$ is the volume of the spherocylinder of approximate effective diameter λ.