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 \(\tau\), and bond-orientational order parameters \(\Psi_n\), with \(n = 4, 6, 12\), along with the \(P^{\ast} - \rho^{\ast}\) 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 \(L/\lambda \approx 7.4\)) 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 \(0.34 \leq \eta \leq 0.45\) \([1]\), whereas for the SS-SCs with \(L/\lambda = 7.4\), the \(N\) phase appears to be stable in the range \(0.30 \leq \eta \leq 0.46\).

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 \(\hat{n}\) are computed. The nematic director \(\hat{n}\) is the eigenvector associated to the largest eigenvalue \((S)\) of the tensor

\[
Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{3}{2} \delta_{i\alpha} \hat{e}_{j\beta} - \frac{\delta_{\alpha\beta}}{2} \right],
\]

where \(\hat{e}_i\) is the orientation of particle \(i\), \(\alpha, \beta \in \{x, y, z\}\) and \(\delta_{\alpha\beta}\) is the Kronecker delta. Geometrically, \(\hat{n}\) 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 \(0.92 < \rho_{2D,QC12}^* < 0.95\). 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 \(\Psi_n\), with \(n = 4, 6, 12\), with temperature are tracked. In Fig. 5, we plot the average \(n\)-fold bond orientational order and reduced energy per particle \((\bar{U}/N\epsilon)\) as a function of temperature for the MC-NVT cooling runs of SS-SCs at \(\rho^* = 0.144\) \((\rho_{2D,QC12}^* = 0.93)\). 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 random tiling 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 \(1.5 \times 10^7\) 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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The order parameters $\tau$ and $\Psi_n$ (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. 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 $\tau$ and $\Psi_n$ (with $n=4, 6$ and 12), characterizing the smectic order and in-plane symmetry, respectively, are included.
FIG. 2: Continuation of Fig. 1.
FIG. 3: Isotherm of the EOS of SS-SCs with a length-to-diameter ratio $\frac{L}{\sigma} = 10$ and shoulder width $\frac{\lambda}{\sigma} = 1.35$ at $T^* = 0.12$, obtained by expansion runs using $N = 1600$ particles. The global nematic ($S$) and smectic ($\tau$) 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 $\Psi_n$ (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).
[8] The packing fraction is defined as $\eta \equiv \rho \nu_{\text{sc}}$, where $\nu_{\text{sc}} = \pi (\lambda/2)^2 [(4/3)(\lambda/2) + L]$ is the volume of the spherocylinder of approximate effective diameter $\lambda$. 