Two Dimensional Ordered Porous Patterns by Molecular Design

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Supporting information

Supporting information includes a description of the algorithm used for cluster analysis and a more detailed analysis of the molecular organization close to the phase transition by means of radial pair correlation functions.

• Cluster analysis

A refined, agglomerative hierarchical clustering algorithm was used for cluster analysis with the Euclidean interparticle distance as the distance metric. The condition for considering two different particles as members of the same cluster was that the distance between them had to be less or equal to $r_{shell}/2$. Should a third particle have been in the vicinity of one of these two particles, it

was also considered a member of the cluster. The above procedure allowed for one-particle clusters (unpaired particles) too.

After all particles were assigned to clusters, all two- and three-particle clusters were reexamined with strict requirements on the range of values for the angle $\varphi_{ij} \equiv \cos^{-1}\left(\mathbf{y}_i \cdot \mathbf{y}_j\right)$ between particles i and j belonging to them. The molecular y-axis is the axis perpendicular to the flat side of the particle which coincides with the particle's radius. Specifically, in the case of two-particle clusters, the angle between the two particles had to be less than 30 degrees and the distance had to be less than $r_{shell}/4$. In the case of three-particle clusters, no more than one angle formed by each pair of particles was less than 70 or greater than 120 degrees. The aforementioned values were chosen for the clustering process to be illustrated in the clearest possible way.

• Pair correlation functions

For the structural characterization of the simulated phases, several pair correlation functions were calculated. The simplest one is the orientationally averaged radial correlation function $g(r)$ which gives the probability that two particles are separated by a distance between $r - dr/2$ and $r + dr/2$. It is defined as $g(r) = \left\langle \delta\left(r - r_{ij}\right)/\rho \right\rangle_{ij} / 2\pi r$, where r_{ij} is the distance between molecules i and j and $\rho = N/A$ is the number surface density with A denoting the surface area of the simulation box. Here $\langle \cdots \rangle_{ij}$ represents ensemble average of the bracketed function with respect to all possible molecular pairs. Orientational radial pair correlation functions were also calculated in the course of the simulations. An informative set of such, distance dependent,

orientational correlation functions was defined as $g_m(r) = \left\langle \delta(r_{ij} - r)\cos(m\varphi_{ij}) \right\rangle_{ij} / \left\langle \delta(r_{ij} - r) \right\rangle_{ij}$ for $m > 1$. In the absence of long range orientational correlations, i.e. for the orientationally disorderd isotropic phases, the functions $g_m(r)$ exhibit significant structure only up to distances of a few molecular diameters (due to the strong orientational anisotropy of the intermolecular potential) and decay rapidly to zero for longer distances. In the case that the system exhibits either long or quasilong orientational order, the long distance behavior of the functions $g_m(r)$ indicates the range and the symmetry elements of the orientational order. All distances were scaled with $\sigma_0 / 2$.

We present radial correlation plots for the systems of particles with thick ($\chi = 0.17$) and thin ($\chi = 0.50$) shell, calculated at pressures slightly above and bellow the phase transition pressure of each system. In the case of the moderate ($\chi = 0.24$) shell system the respective radial correlation plots were calculated at a very low and very high pressure since a phase transition was not apparent. To facilitate the analysis of molecular correlations with the use of such plots, we also provide a representative snapshot of the system under consideration with the supramolecular clusters colored according to their population (and thus shape, see previous section on cluster analysis). The following color code has been used: red, yellow, blue, dark grey, magenta for one to five particle aggregates, respectively.

Thick shell systems

The low pressure plot of $g(r)$ indicates clearly that significant positional correlations start to develop as the system is compressed from the isotropic state. What mainly differentiates the low from high pressure plot of $g(r)$ is the merging of the first two peaks present in the former, into a

single peak in the high pressure state. This is a clear signature of the clustering nature of the phase transition. The two first peaks in the isotropic state reveal that close to the phase transition, molecular aggregates with different but well defined shapes were already formed in accordance with the corresponding snapshot. These two peaks merge into one peak in the ordered phase, located at a distance compatible with the formation of four-particle molecular clusters.

Just above the phase transition pressure, the peaks of $g_m(r)$ for $m = 2,3,4$ (red, green and blue colored lines, respectively) at first and second nearest neighbor distances (both of which contribute to the first peak in $g(r)$ plot) hint to the presence of three- and four-particle clusters, a

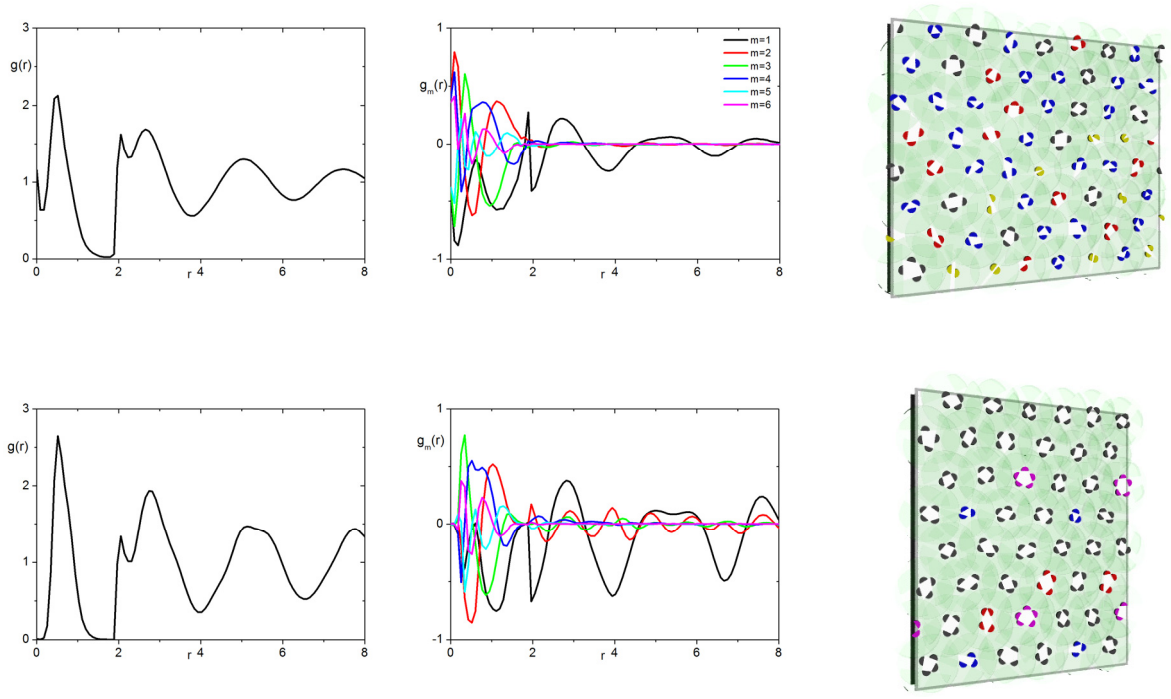

Figure S1. Radial (left column), orientational (middle column) correlation functions and snapshots (right column) of the thick shell system ($\chi = 0.17$) at $p^* = 6.0$ (top row) and $p^* = 7.4$ (bottom row). The phase transition pressure for this system is $p^* \simeq 6.8$.

fact which is also verified by inspecting the respective snapshot.

Moderate shell systems

At the high pressure state, strong positional correlations are present as the $g(r)$ plot shows. The intense peak of $g(r)$ at a separation distance of around $2r_{core}$ together with the intense peaks at the same distance of $g_3(r)$ and $g_6(r)$ (green and violet colored lines, respectively) sketches clusters with the cores of the particles forming a triangle. This is nicely confirmed by the respective snapshot. On the other hand, in contrast with the thick shell system, the near neighbour

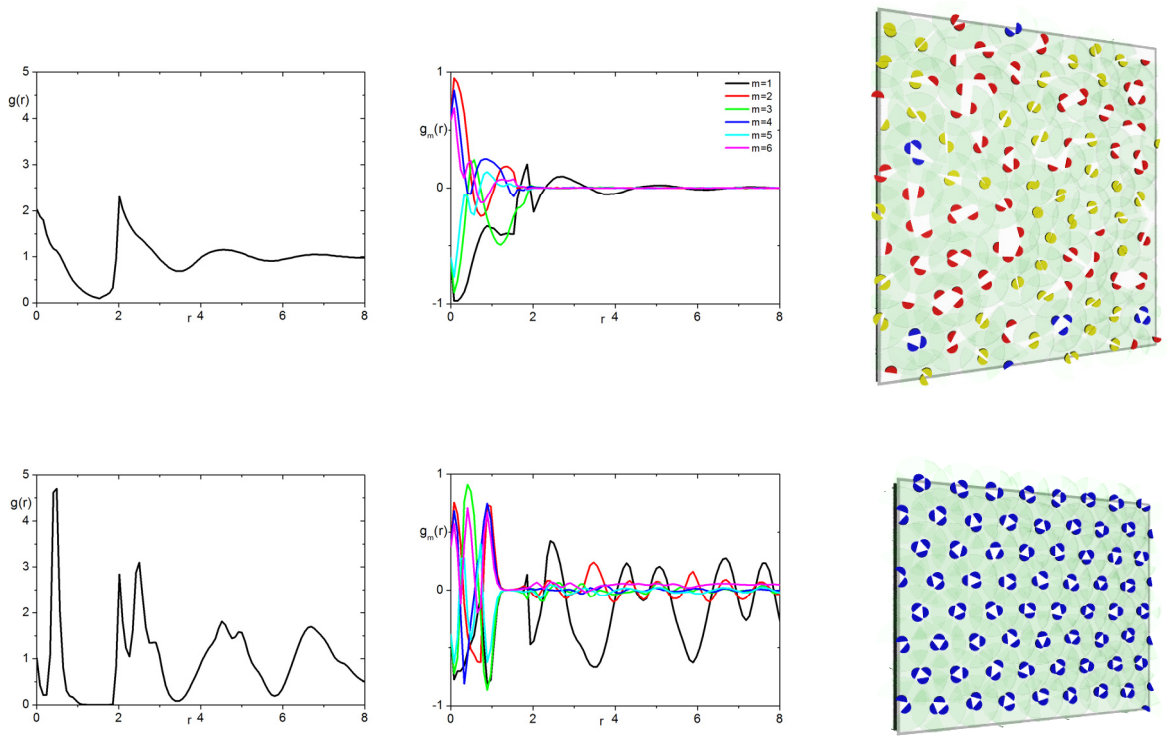

Figure S2. Radial (left column), orientational (middle column) correlation functions and snapshots (right column) of the moderate shell system ($\chi = 0.24$) at $p^* = 4.5$ (top row) and $p^* = 14.5$ (bottom row).

interparticle distances show a broad distribution between 0 and σ_0. This is in accordance with the cluster plot (Figure 4b in the paper) and reveals that the short-range positional correlations alone cannot give a clear picture of cluster formation in the isotropic phase. This broad distribution of distances in the isotropic phase transforms into a single, well defined, peak in the high pressure phase.

Thin shell systems

The coincidence of the broad peaks of all the different $g_m(r)$ together with a peak in $g(r)$ at separation distances close to zero suggests the formation of two-particle aggregates at pressures close to and below the phase transition pressure. The second peak at a separation distance equal to the sum of the core and shell radii also suggests a deformed hexagonal lattice. Since the aggregates are disk like in shape, they are able to freely rotate as a whole and this explains the absence of long range orientational correlations.

Just above the phase transition pressure, the shape of $g(r)$ is characteristic of a hexagonal lattice and at higher pressure coincides with the shape of the respective radial correlation function of a hard disk system composed of disks with diameter σ_0.

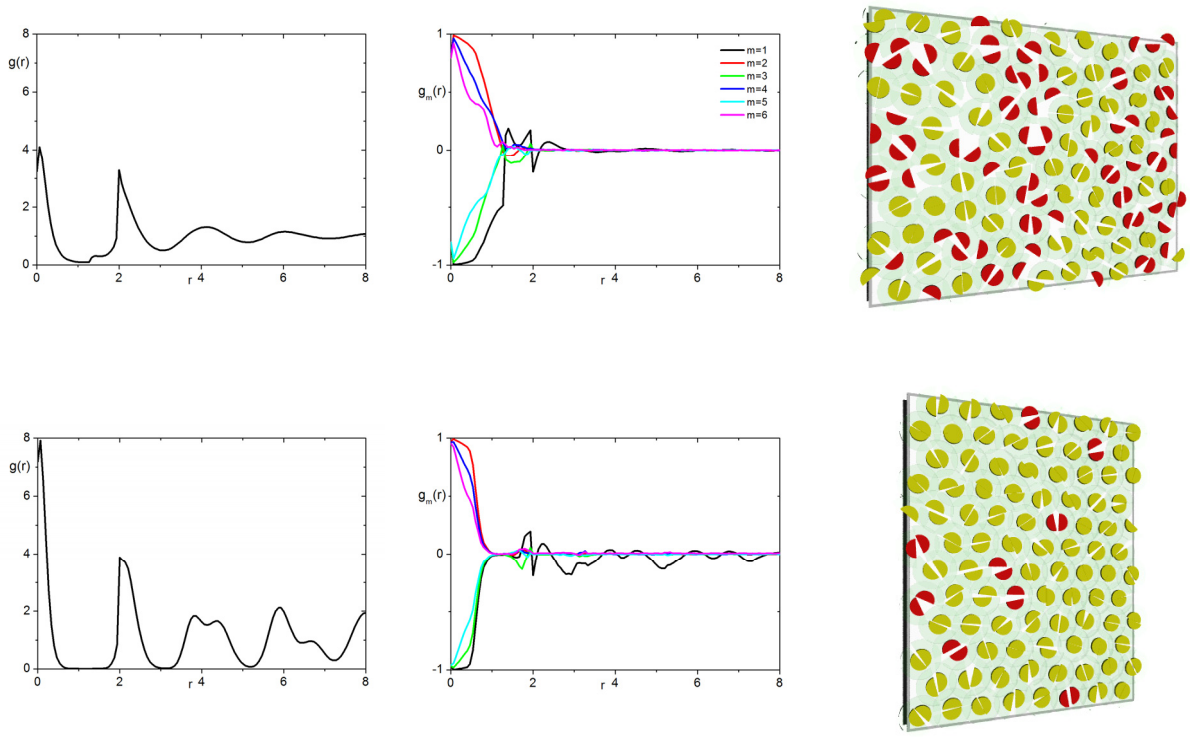

Figure S3. Radial (left column), orientational (middle column) correlation functions and snapshots (right column) of the thin shell system ($\chi = 0.50$) at $p^* = 6.4$ (top row) and $p^* = 7.9$ (bottom row). The phase transition pressure for this system is $p^* \simeq 7.0$.