Electronic Supplementary Material (ESI) for Soft Matter

Self-assembly scenarios of patchy colloidal particles - supplementary information

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Orientational reference Hamiltonian

When calculating free energies of systems consisting of anisotropically interacting particles *via* the Frenkel-Ladd method, the reference Hamiltonian includes an orientational term. The contribution to the entropy stemming from the orientational degrees of freedom can be accounted for by integrating to a reference Einstein crystal in which the particles are coupled to an orientational field that tends to align the particles with the same orientation as in the solid structure under study. It is usually convenient that the orientational field exhibits the same symmetry as the particles[1]. Therefore we used two different orientational fields for each of the geometries of the particles for which the phase diagram at finite T was computed. For the perfect tetrahedral case (with T_d symmetry), the orientation of each particle in the reference structure can specified by two unitary vector $\mathbf{a_0}$ and $\mathbf{b_0}$ that are colinear with any two specified patches, and the orientational field is defined as:[1,2]

$$U_{\text{orient}} = \sum_{i=1}^{N} \lambda_o \left[\sin^2 \left(\Psi_{a,i} \right) + \sin^2 \left(\Psi_{b,i} \right) \right] \tag{1}$$

where λ_o is the coupling parameter, which has units of energy, and $\Psi_{a,i}$ ($\Psi_{b,i}$) is the angle formed by the closest patch in the instantaneous orientation of molecule i and the vector $\mathbf{a_0}$ ($\Psi_{b,i}$) in the reference structure. The particles with $g \approx 127.50$ have C_{3v} symmetry. In this case the orientation of the particles is defined by a vector colinear to the patch at the "north pole" ($\mathbf{a_0}$) and the other is colinear to one of the other three patches ($\mathbf{b_0}$). The orientational field is the defined as:

$$U_{\text{orient}} = \sum_{i=1}^{N} \lambda_o \left[\left(\frac{\Psi_{a,i}}{\pi} \right)^2 + \sin^2 \left(\Psi_{b,i} \right) \right] \tag{2}$$

References

1 C. Vega, E. Sanz, J. L. F. Abascal and E. G. Noya, *J. Phys.: Condens. Matter*, 2008, **20**, 153101.
2 E. G. Noya, C. Vega, J. P. K. Doye and A. A. Louis, *J. Chem. Phys.*, 2010, **132**, 234511.

Visual representations of selected ordered equilibrium structures at $T = 0$

In Figures 1 to 4, we display the ordered equilibrium structures identified at $T = 0$ for those systems that are specified in the panels of Figure 2 of the main article by labels "a" to "h". For the convenience of the reader, we repeat here the descriptions of these strucutres provided in the main article.

- "a - open": layered structure with full bond saturation; each layer consists of fully bonded particles, forming a honeycomb lattice; the inter-layer bonding is realized via the patches located at the north poles
- "b - hexagonal layers I": hcp-like structure (i.e., AB stacking of hexagonally arranged layers) which is characterized by rather weak *intra*-layer and stronger *inter*-layer bonds
- "c - bc I": bcc-like configuration; can be seen as two interpenetrating diamond lattices, which only interact *via* mutual repulsion at short distances; the two sublattices are slightly shifted against each other, i.e., particles of sublattice A do not lie exactly in the center of the voids of sublattice B and vice versa, as can be seen in the central left panel of figure 2: the yellow particles would lie exactly on top of the red particles in a perfect bcc lattice
- "d - fc II": compact, almost close-packed fcc-like structure
- "e - bc I": lattice with the same bonding pattern as structure "c" (bcc/double diamond), but slightly different arrangement of the colloidal particles
- "f - bc II": rather closely packed bc-like lattice; the particular patch decoration allows for a high bond saturation: bonds are formed between second-nearest neighbours in the bcc-like lattice, i.e., along the edges of the bcc-like unit cell
- "g - hexagonal layers III": stacking of staggered, hexagonally ordered double layers: each double layer is formed by two congruent hexagonal particle arrangements, bonded to each other via the patch located at the north pole; the double layers themselves are connected via the three patches located at the basis; all bonds are fully saturated
- "h -hexagonal packed III": ABAB... stacking of hexagonally close-packed layers; particles are essentially unbonded within these layers, but establish relatively strong bonds to the neighbouring layers

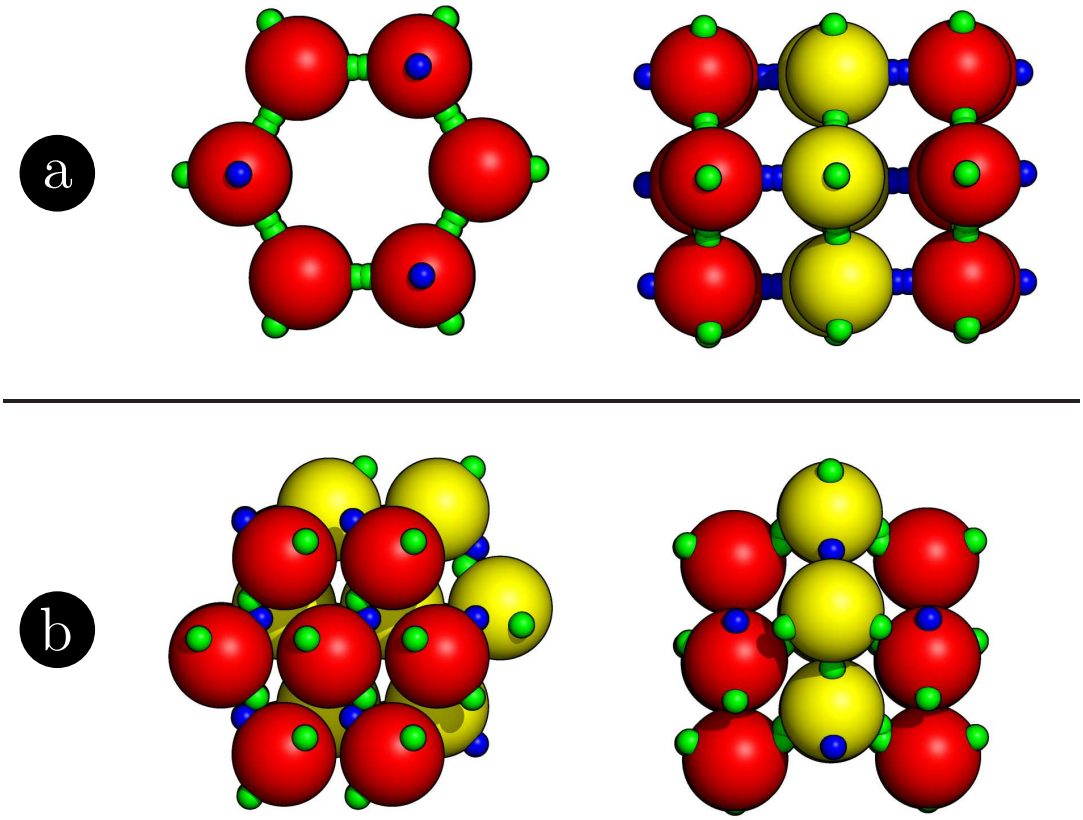

Fig. 1 Perpendicular views of the low-pressure (top) and the high-pressure (bottom) ordered equilibrium structure obtained for $g = 93.75$ (labels "a - open" and "b - hexagonal layers I" in Figure 2 of the main article). The colour code for the blue and green patches has been specified in Figure 1 of the main article, the colours red and yellow for the patchy particles have been introduced for convenience*.

* (i) For layered honeycomb lattices and structures consisting of hexagonal layers, particles located in different layers are coloured in an alternating pattern. (ii) For bcc-like lattices, particles located on the vertices of the cube appear in red, while the particles at the center of the cube are colour yellow. (iii) In the double diamond picture, particles belonging to different non-interacting diamond sublattices appear in different colours. (iv) For fcc-like structures, the particles located at the vertices of the cube and the particles at the centers of the faces of the cube are coloured red and yellow, respectively.

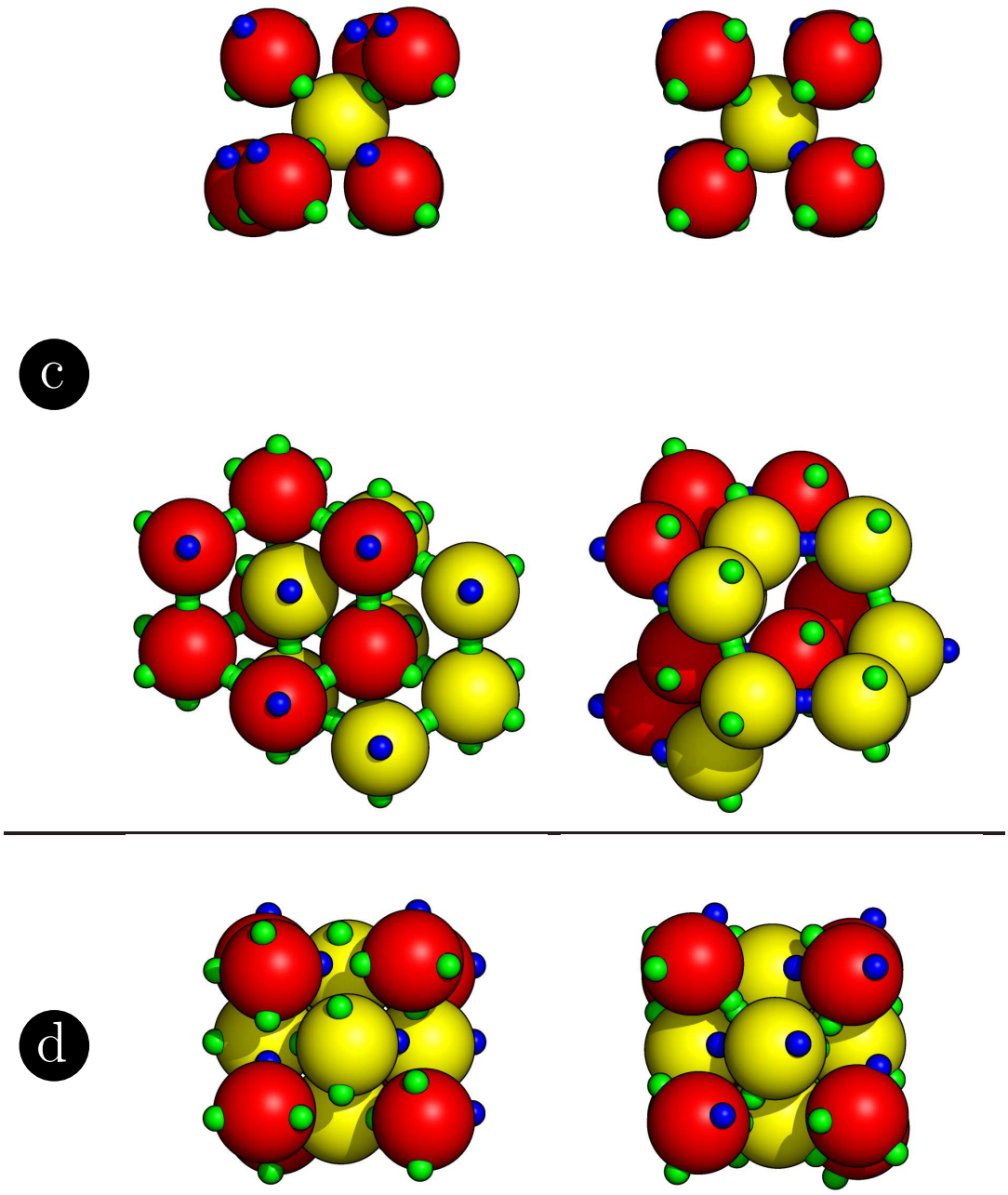

Fig. 2 Perpendicular views of the low-pressure ordered equilibrium structure in the body-centered picture (top) and the double-diamond picture (center) as well as the high-pressure structure (bottom) obtained for $g \simeq 109.47$ (labels "c - bc I" and "d - fc II" in Figure 2 of the main article), corresponding to a regular tetrahedral arrangement of the patches. The colour code for the blue and green patches has been specified in Figure 1 of the main article, the colours red and yellow for the patchy particles have been introduced for convenience*.

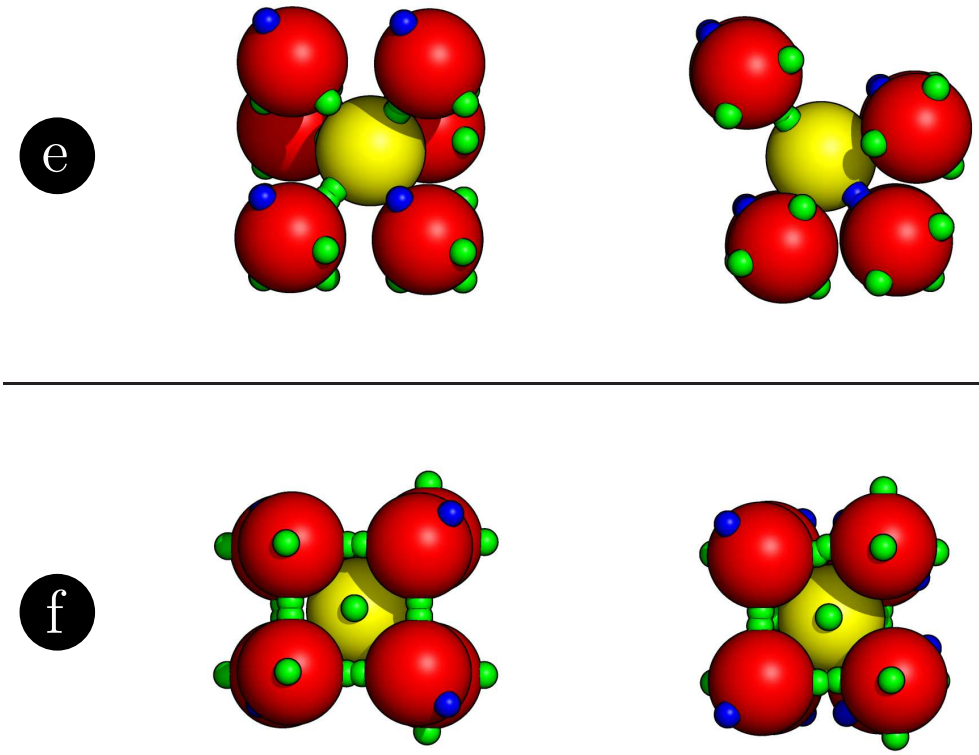

Fig. 3 Perpendicular views of the low-pressure (top) and the high-pressure (bottom) ordered equilibrium structure obtained for $g = 123.75$ (labels "e - bc I" and "f - bc II" in Figure 2 of the main article). The colour code for the blue and green patches has been specified in Figure 1 of the main article, the colours red and yellow for the patchy particles have been introduced for convenience*.

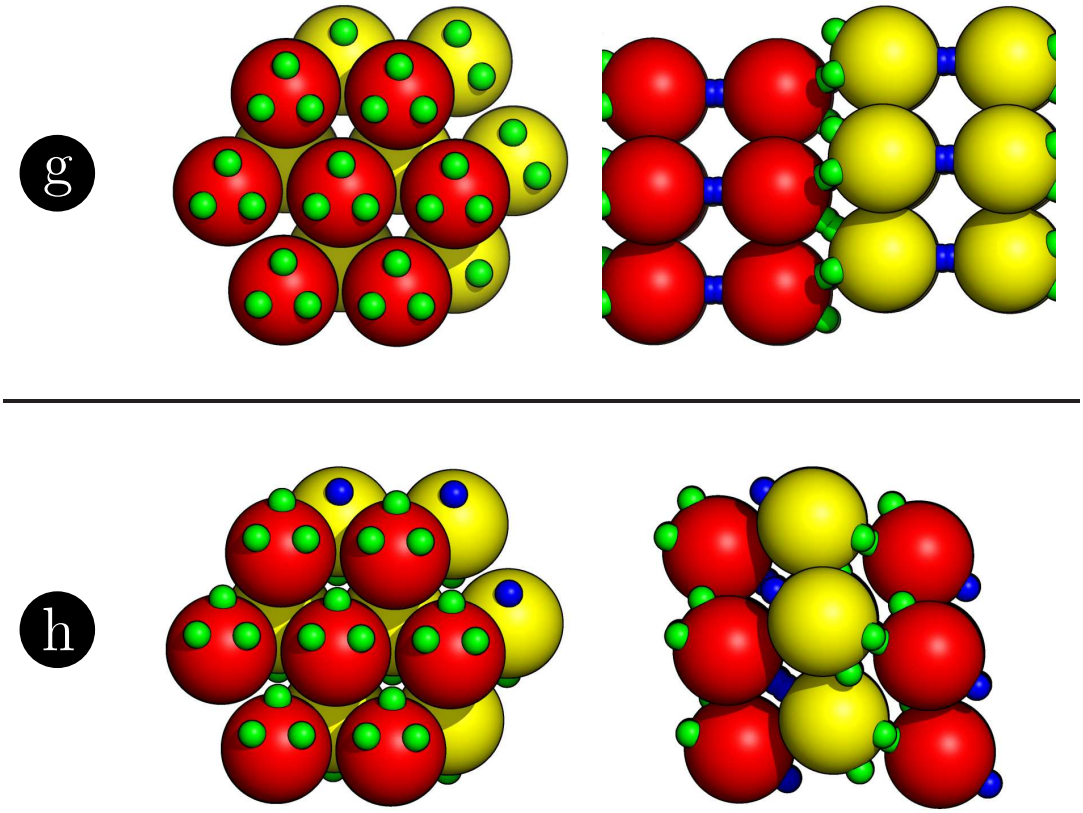

Fig. 4 Perpendicular views of the low-pressure (top) and high-pressure (bottom), ordered equilibrium structure obtained for $g = 150.00$ (labels "g - hexagonal layers III" and "h - hexagonal packed III" in Figure 2 of the main article). The colour code for the blue and green patches has been specified in Figure 1 of the main article, the colours red and yellow for the patchy particles have been introduced for convenience*.