Supporting information of the MS

Layering Transitions in Confined Colloidal Crystals: The *hcp-like* phase

by

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The Fig. 1S shows the well-known transition $1\Delta \rightarrow 1B \rightarrow 2\square$. This transition will help us to understand the same transition in the next stage of n monolayers, for n small values.

For equal values of thickness and spheres diameter, maximun packing fraction corresponds to a triangular facet (1Δ) monolayer of the (111) fcc structure (a).

Then, as the height of the confined sample increases, a buckled phase appears (b). Such a buckling mechanism maximizes the packing fraction between one and two layers. Indeed, as it can be seen in inset of Fig. 3S (b), one zone with two sublayers of different height is generated and, a two-layer structure begins to be formed. By changing the magnitude of the vertical displacement of the sublayers, the buckling phase can easily adapt itself to the gap of the wedge cell, and therefore maximizing the filling fraction value.

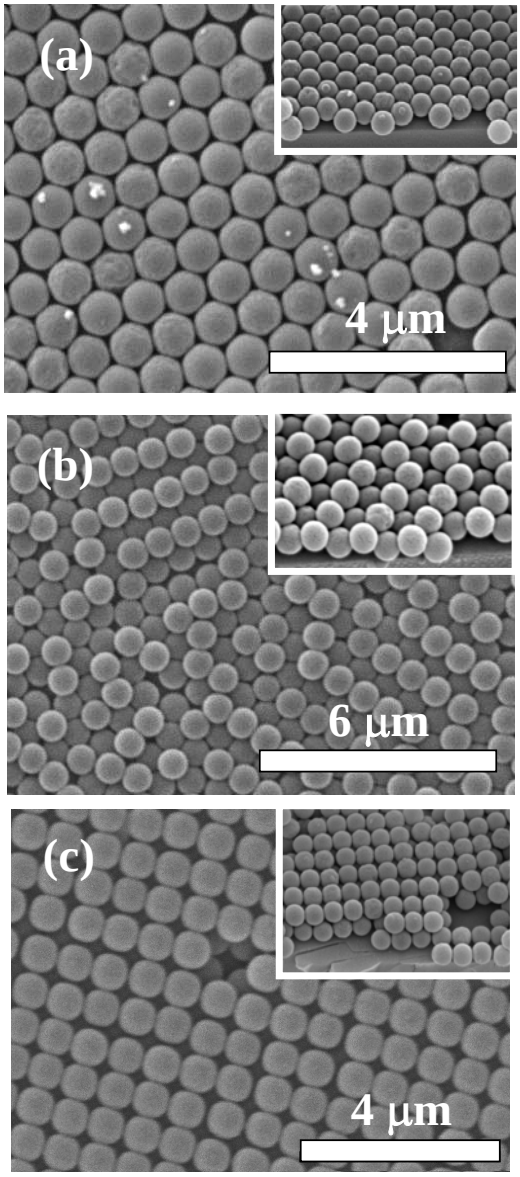


Fig. 1S. SEM images of the transition between 1Δ (a) and 2□ (c). (b) Buckling phase. Inset: Side view images.

The Fig. 2S shows a SEM image of the transition 2□ → 2Δ. The transition takes place very rapidly, and consequently the rhombic phase appears in a very restricted spatial region not able to be monitorized optically. This picture is very similar to that shown by Pieranski *et al* (Fig. 3f from Ref. 1 of the MS) and simulated by Schmidt and Löwen (ref. 9 of the MS).

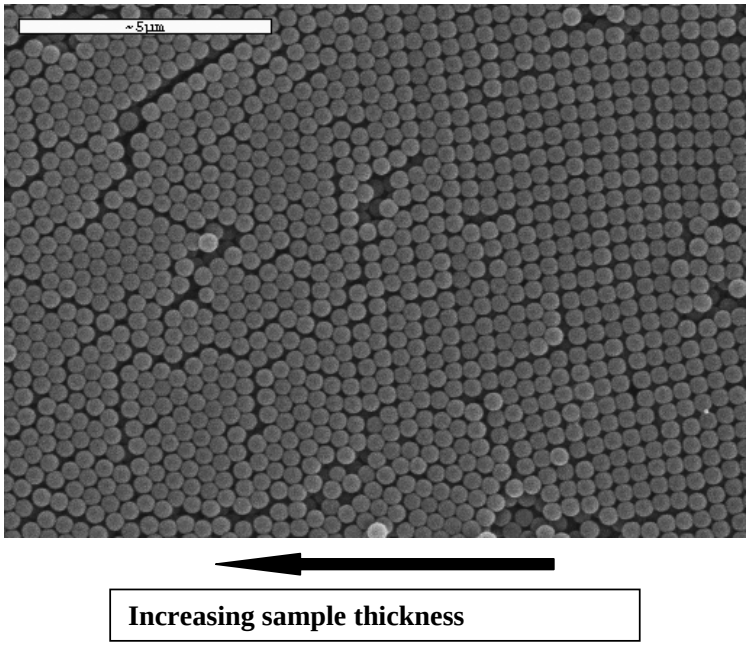
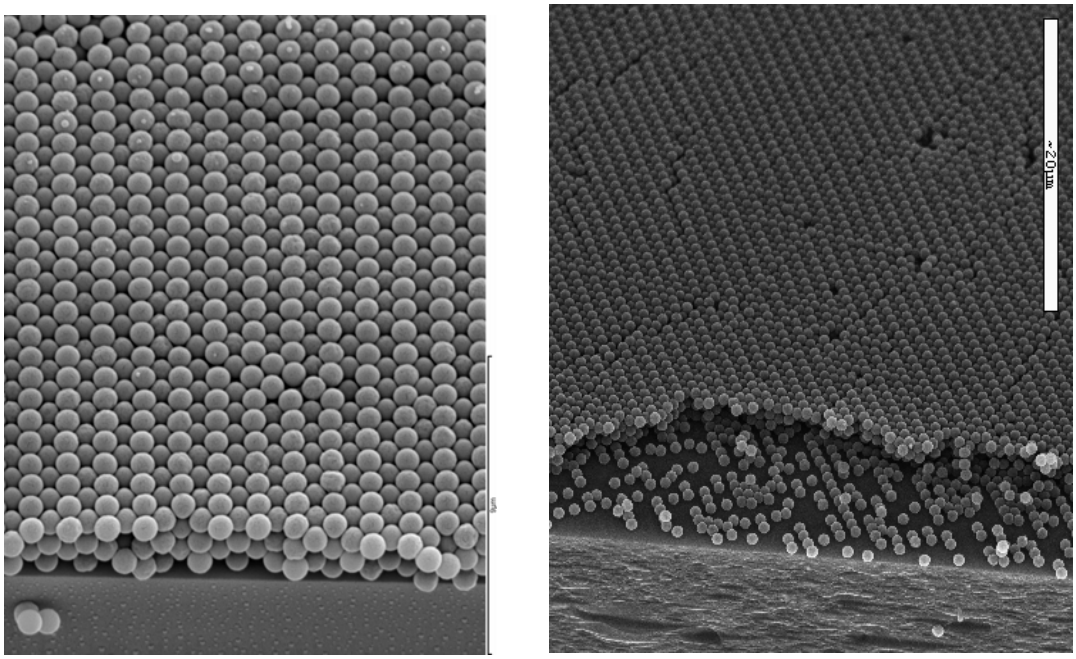


Fig. 2S. SEM image of the transition 2□ → 2Δ.

Fig. 3S shows a low magnification SEM images of the *hcp-like* phase. The bar of the top right image corresponds to 20 μm. Bottom SEM image shows a l*arge sample area fully arranged in the hcp-like phase. The top bar corresponds to 50 μm.* It shows large and stable hcp-like domains.



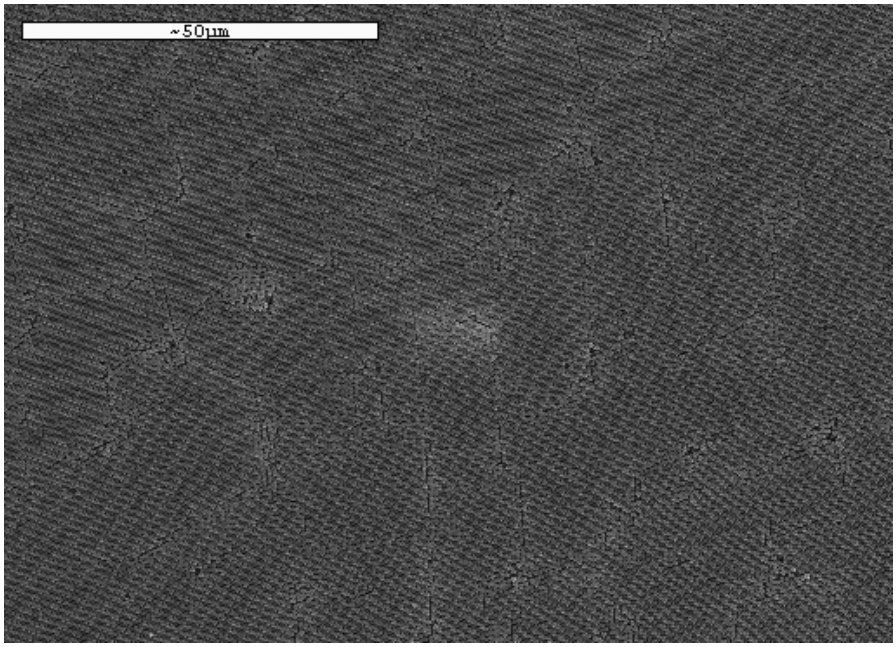
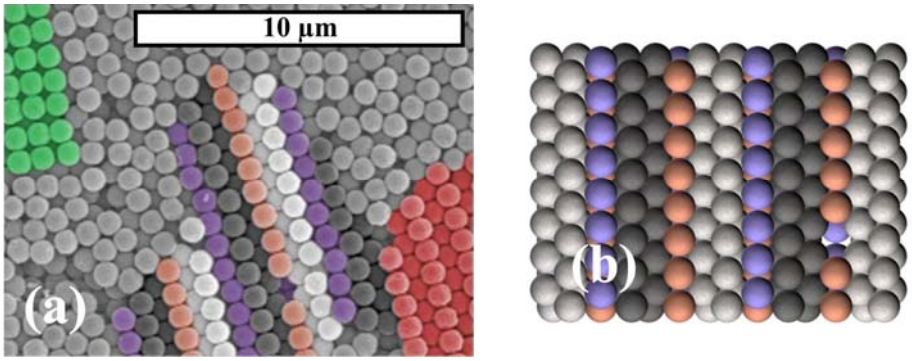


Fig. 3S. SEM images with different resolution values showing the high stability of the hcp-like phase.

Figure 4S shows a SEM image of the *pre 3□* intermediate that appears in the transition between the 3hcp-like phase (model (d) in figure 2) and the 3□ (model (f) in figure 2). We also show the packing model (b) if this intermediate phase. The spheres have been colored according to those of the model to help the reader identifying such phase.



Con formato: Justificado

Figure 4S (a). SEM image of the intermediate phase pre 3□ that appears between the 3 hcp like at the bottom right part (colored in red) and the 3□ (colored in green) at the top left part of image. Figure 4S (b) shows a packing model of the pre 3□ .

Fig. 5S shows a SEM image of the top view of the hcp-like phase. The missing sphere in one row allows to see the ordering of the underneath layer. It can unambiguously be ascribed to the *hcp-like* phase.

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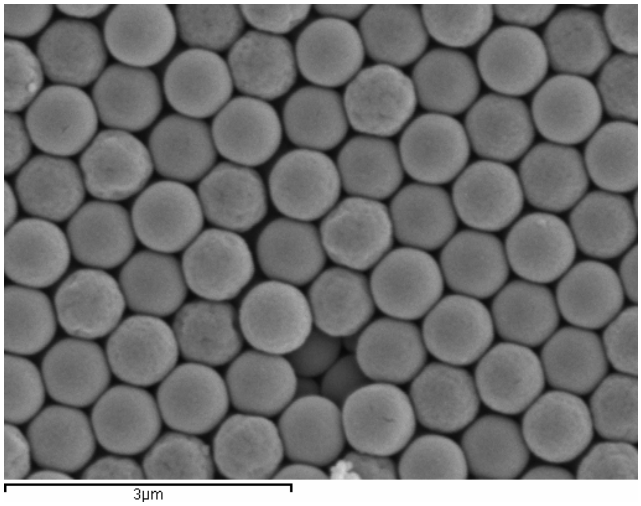

Fig. 5S. SEM image of the hcp-like phase