# Surprising Self-Assembly of Hard Spheres and Long-Ranged Repulsive Rods in Confinement

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**ABSTRACT**: In research aimed at making colloidal crystalline supraparticles by having monodisperse spherical nanoparticles crystallize in slowly evaporating oil emulsion droplets we discovered icosahedral symmetry in the resulting dried colloidal crystals [1]. Subsequent work with different kind of nanoparticles and a similar study using micron-sized silica colloids all confirmed that crystallization of hard spheres in a spherical confinement results in crystals with an icosahedral symmetry, which is known not to be able to regularly pack in 3D space, up until roughly 100.000 particles. Computer simulations confirmed the experimental observations and were able to also show that indeed for roughly this number of particles or less the free energy of icosahedral packings is lower than that of an FCC crystal. Moreover, the simulations also provide clues to the actual crystallization pathway/mechanism [1].

Micron-sized and fluorescently labeled rod-like silica colloids [2,3] were recently found in our group to form so-called rotator phases or plastic crystals if the Debye screening length was made sufficiently large (~particle length) [4]. In a plastic crystal positions are long-ranged and ordered on a 3D lattice, while rotations are still free and therefore orientational order is short-ranged or even absent. When such systems are confined between two charged flat walls we find alternating 3D ordinary and plastic crystal phases as function of the plate-plate separation. This surprising sequence was found to originate from subtle differences in the charge repulsions between the rods themselves and a rod with the wall.

1) *Entropy-driven formation of icosahedral colloidal clusters by spherical confinement,* Bart de Nijs, Simone Dussi, Frank Smallenburg, Laura Filion, Arnout Imhof, Marjolein Dijkstra, Alfons van Blaaderen, ***Accepted Nature Materials*** (2014).

2) Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio, A. Kuijk, A. van Blaaderen, and A. Imhof, *JACS* **133**, 2346-2349 (2011)

3) Colloidal Silica Rods: Material Properties and Fluorescent Labeling, A. Kuijk, A. Imhof, M. H. W. Verkuijlen, T. H. Besseling, E. R. H. van Eck, and A. van Blaaderen, *Particle **31**, 706-713* (2014).

4) Switching plastic crystals of colloidal rods with electric fields, B. Liu, T. H. Besseling, M. Hermes, A. F. Demirörs, A. Imhof, and A. van Blaaderen, *Nature Communications* **5**: 3092 (2014).

**ALL ARE WELCOME!!!**