Supplementary Materials

1 Figures and Movies captions

1.1 Crystal nucleation - Supplementary Movie 1

This movie file shows simple cubic crystals nucleating from silica cubes dispersed in water containing 0.8 g/L of poly(ethylene oxide) with molecular weight of 600,000. Single particles are driven together by depletion forces to larger crystallites. The movie was acquired at 0.5 fr/s and it is displayed at 10 fr/s.

1.2 Crystal melting - Supplementary Movie 2

This movie file shows crystallites of silica cubic colloids prepared using poly(*N*-isopropylacrylamide) (pNIPAM) microgel particles as depletants. At 40 °C pNIPAM particles shrink causing a reduction of the depletion attraction sufficient for the crystals to gradually melt. The particles where allowed to crystallize at room temperature (20 °C) and then the temperature was slowly increased until all the crystallites melted ($\sim$45 °C). The movie was acquired at 2 fr/s and it is displayed at 10 fr/s.

1.3 Crystals coalescence-Supplementary Figure 1

a, Optical microscope pictures showing crystallites of silica cubic colloids assembled in the presence of 0.8 g/L of poly(ethylene oxide) with molecular weight of 600,000 taken after 4 days from the sample preparation. The irregular shape of the crystals is due to the coalescence of smaller units to form larger structures as shown in the pictures of panel **b**. Following this mechanism, the crystals grow even further as shown in panel **c** for an 8 days old sample. The crystals do not grow indefinitely because of the tendency of the polymer to adsorb on the particles' surface in time and consequently suppressing depletion interactions. Scale bar, 20μm.

2 Particle Shape

As can be seen in Fig. 1 (main text), the corners of the cubic particles are rounded. In this section we characterize this rounded shape by fitting superellipsoids to it. A superellipsoid is determined by the locus of:

$$\left(\frac{x}{a}\right)^m + \left(\frac{y}{b}\right)^m + \left(\frac{z}{c}\right)^m = 1. \tag{1}$$

For $a = b = c = r$ and $m = 2$, x, y, z lie on a sphere and for $a = b \neq c$ and $m = 2$ x, y, z lie on an ellipsoid of revolution. Fo $m \rightarrow \infty$ these shapes become a cube and a rectangular block respectively. The value of m can therefore be used to characterize the roundedness of the shape and the relative magnitudes of a, b and c to characterize deviations from cubic symmetry.

To determine the parameters that characterize the shape, we took as a starting point TEM images, such as shown in Fig. 1. We then used a standard algorithm to find the edges of the cubes, and fitted an angular form of equation 1. A typical fit is shown in Fig. 1. A Plot of the result of fitting an ensemble of images is shown in Fig. 2. Fitting to a collection of images suggests a mean value of $m \sim 3.5$ and polydispersity in the aspect ratio of a few %.

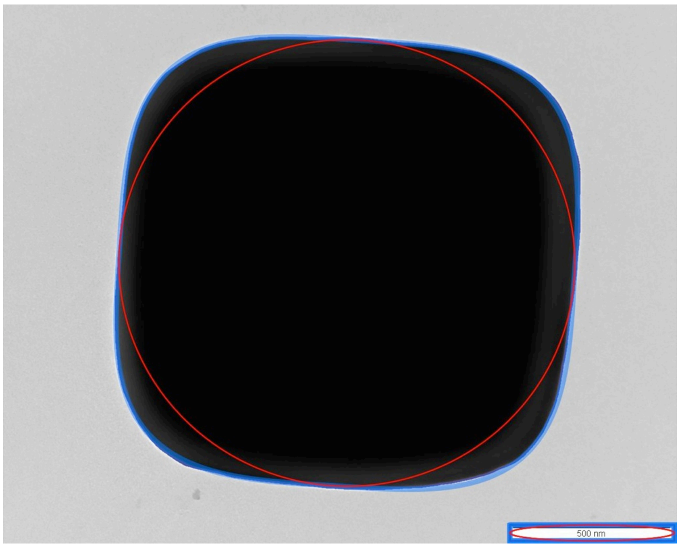

Figure 1: A TEM image of a superball with overlaid (blue) the edge and our fit to it and (red) the corresponding shape with $m = 2$.

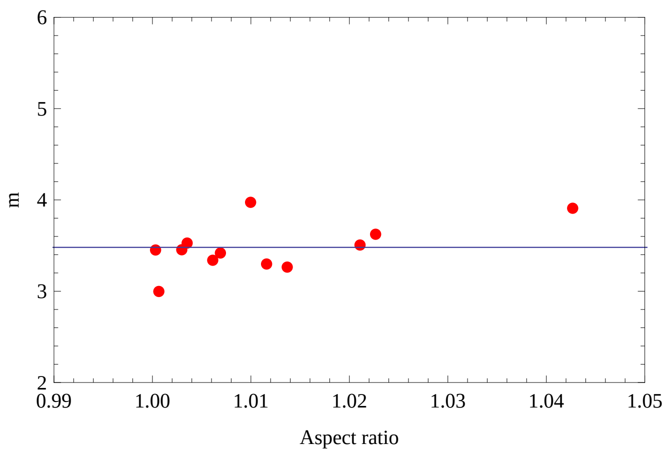

Figure 2: Fitting to a collection of images indicates a mean value of $m \sim 3.5$ and polydispersity in the aspect ratio of $1 - 2\%$.

3 Particle Tracking

To track the cubic particles, we make use of the fact that their edges have some thickness and therefore overlap with a circle. We first filter the image using a bandpass filter (Fig. 3 **a**), followed by a sequence of Hough circle transforms to determine the centers and radii of the cubes (Fig. 3 **b**). The orientation of each cube can be determined either by considering a region around the center of each cube and comparing it to rotated templates by subtraction, or by triangulation. Fig. 3 **d** shows cubes whose orientation was determined by triangulation as follows: we computed the nearest neightbours of each cube by delaunay triangulation and subsequently selected the 4 nearest neighbors these are shown in Fig. 3 **c**. From these, the tetratic order parameter was computed as $\psi_4 = \frac{1}{4}\sum_{i=1}{}^{4}\exp^{i4\theta}$ where θ is the angle of each bond. The oriantation of the cube is then given by ϕ=1/4 arg(ψ_4).

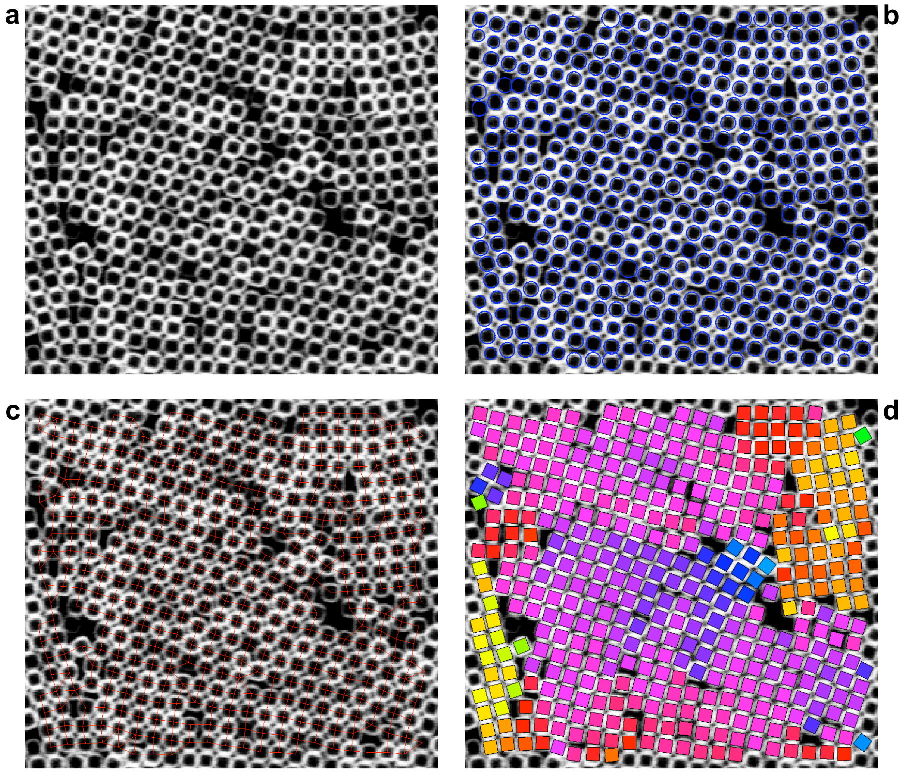

Figure 3: Overview of the four steps involved in the particle tracking: after the image is filtered (**a**) the centers of the particles are located using Hough circle transforms (**b**), subsequently four nearest neighbors are assigned to each particle (**c**) and then the orientation of each cube is determined (**d**).