Supplementary Information

Real-space imaging of translational and rotational dynamics of hard spheres from the fluid to the crystal

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Materials and methods

Chemicals

Reagents used for polymethylmethacrylate particles/shell growth. Methyl methacrylate (MMA), methacrylic acid (MA), ethyl acetate (EA), butyl acetate (BA), azo-bis-isobutyronitrile (AIBN), dodecane and octylmercaptane were purchased from Sigma-Aldrich, Germany and used as received except for MMA which was purified by filtration over basic aluminium oxide (Woelm Pharma, Germany) to remove the inhibitor. Hexane was purchased from Fluka, Germany and used as received.

Reagents used for fluorescence labeling. Rhodamine B-4-vinylbenzylester (RhB-4V) was synthesized from Rhodamine B and 4-vinylbenzyl alcohol via Steglich esterification. Quasar 670 Carboxylic Acid (Q670) was purchased from Biosearch Technologies, USA and modified by esterification with 4-vinylbenzyl alcohol.

Reagents for microscopy measurements: cis/trans-decahydronapthalene (decalin) and Cyclohexylbromide (CHB) were purchased from Sigma-Aldrich, Germany and used as delivered.

Synthesis of PMMA/PMMA core-shell particles

Fluorescent dye-labeled PMMA microparticles were prepared as described by Antl and co-workers.[1] These particles were used as seeds onto which a PMMA shell was grown with a similar dispersion polymerization step. Approximately 0.4 – 0.6 g of the seed particles were dispersed in 0.3 g dodecane and 0.6 g hexane. 70 mg AIBN was added and dissolved under heating to 93°C. 16 µl of octylmercaptane was added under nitrogen atmosphere. 6 mL of a monomer mixture consisting of 10.03 g MMA, 0.2 g MA, 7 g Hexane, 3.5 g dodecane and 1.2 g steric stabilizer (PHSA-g-PMMA brush copolymer)[2, 3] solution (5% in butylacetate/ethylacetate (1:2) (w/w)) were added with a syringe pump within 2 hours and stirred for one hour at 93°C. The mixture was cooled to room temperature and washed several times with hexane.

Covalent locking of the steric stabilizer

To lock the stabilizer on the surface of the colloids, 1 mg of N,N-dimethyldodecylamine for every 100 mg of colloids were added to a dispersion of colloids. The colloids were first dispersed in dodecane with concentrations of approximately 1% (w/w). The reaction mixture was stirred at 120 °C in an oil bath for one hour. After cooling, the colloids were washed once with hexane. To prevent any side reactions of the fluorescent dye, this procedure was performed under nitrogen atmosphere.

Particle size distribution

To determine the amount of particle clusters generated and the dispersity of the colloids, we analyzed SEM images with a magnification of approximately 700 – 2000 and used the particle analyzer tool provided by Image J®. With this tool, binary images can be analyzed to find spherical objects and determine different parameters, like circularity, long and short axis and others. The long axis diameter was used to generate histograms of the size distribution and distinguish the polydispersity by taking standard deviation values of cluster size distributions. SEM images are converted in a binary image, a watershed filter was used to separate single particles and the scale set of the image (pixel size). The particle analyzer function was used to get a table of all

occurring particle sizes. The particle distribution of the host particles is shown in Fig. S1. The maximum is at 4.60 µm, with a standard deviation of 0.135, resulting in a dispersity index of the particles of 1.03.
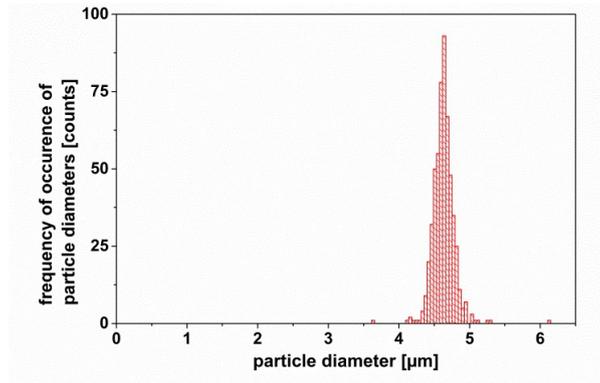

Fig. S1: Histogram of particle diameters detected with the SEM image analysis.

Volume fraction stability

To check the stability of the volume fraction over the duration of the measurements and to see if sedimentation did not play a role, we calculated the volume fraction for each time step of the samples. Fig. S2 shows typical plots of the volume fractions versus time for four different samples. No indication for sedimentation is found.
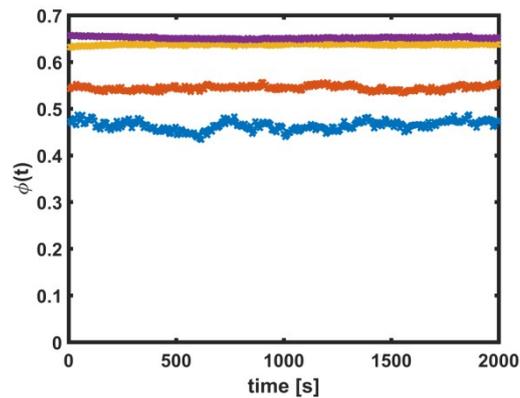

Fig. S2: Volume fraction as a function of time during four different measurements. No signs of sedimentation are observed.

Fourier Transform Analysis

In order to determine the phase of the sample, 2D slices of the samples were inspected and Fourier transforms of the respective images were calculated with ImageJ (Fig. S3). Appearance of single bright spots was interpreted as the occurrence of sample regions with crystalline order. In the samples at volume fractions higher than $\phi = 0.54$, only crystalline phases were observed.
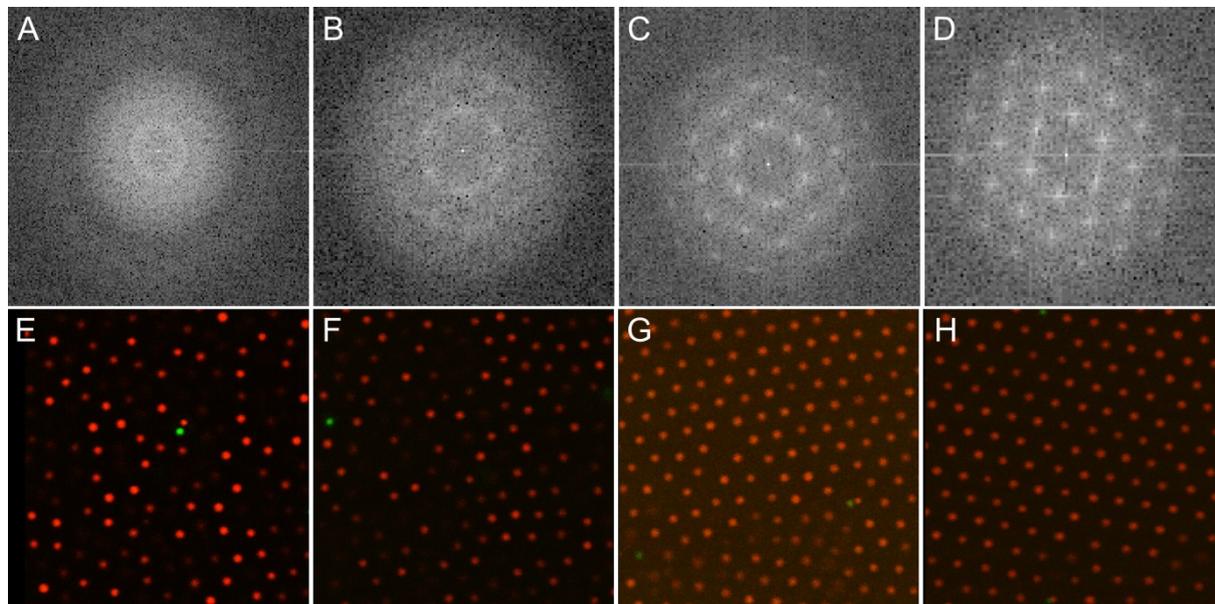

Fig. S3: Fourier transforms (A-D) of microscopy images (E-H) of samples at different volume fractions ranging from the liquid to the crystal. (A,E) $\phi = 0.50$ (B,F)) $\phi = 0.51$ (C,G) $\phi = 0.53$ and (D,H)) $\phi = 0.55$.

References

1.   L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth and J. A. Waters, *Colloid Surface*, 1986, **17**, 67-78.
2.   K. E. J. Barrett and Imperial Chemical Industries ltd. Paints Division., *Dispersion polymerization in organic media*, Wiley, London, New York, **1974**.
3.   M. T. Elsesser and A. D. Hollingsworth, *Langmuir*, 2010, **26**, 17989-17996.