![ESRF logo]	**Experiment title:** Role of bond ordering on the crystallization process of hard sphere colloids	**Experiment number**: SC-3531
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Report:

Until now it is believed, that the crystallization process is primarily controlled by positional ordering. However, recent molecular dynamics simulations [1] and micrsoscopy [2] studies proposed that bond orientational ordering can play a key role in this process. It was found that orientational bond order is observable in a first pre-crystallization step. Afterwards, positional order leads to crystallization. The positional ordering gets easily destroyed even by weak frustration such as polydispersity and anisotropic interactions which favors symmetries not consistent with that of the equilibrium crystal.

In experiment SC-3531 we studied the orientational order in colloidal hard sphere systems in around the crystalline phase. Hard sphere colloids are used to mimic the phase diagram of simple liquids, its phase depends on the volume fraction φ only [3]. With increasing particle polydispersity the stability region of the crystal phase shifts to higher volume fractions, whereas for polydispersities above approx. 0.07 no crystal phase can be formed [4].
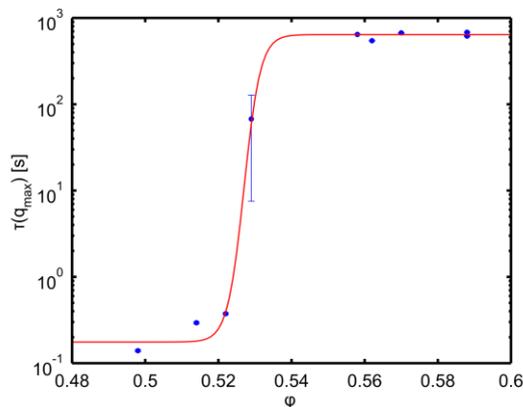

Figure 1: Relaxation times at maximum of S(q). Red line is a guide to the eye.

In this experiment, we studied hard sphere systems (PMMA dissolved in decalin) at volume fractions between 0.50 and 0.59. The polydispersity of the particles was slightly below 0.07 so that the sample was able to crystallize. As during the experiments no crystals were observed, the corresponding samples were measured at "supercooled" conditions. For every sample first an XPCS run was measured to determine the dynamics of the sample. After that, speckle patterns were measured at approximately 1000 different spots on the sample, at each spot at least 10-20 patterns were taken to check for consistency. These patterns were analyzed according to the X-ray cross correlation (XCCA) scheme (for details see [5]). The sample order is reflected by the

cross correlation function $\Psi(l,q)$. A dominant order in the sample is expressed by maxima of $\Psi(l,q)$, e.g. a dominant hexagonal order would result in maxima for $l=6$ and $l=12$.

Fig. 1 shows the relaxation times at the maximum of $S(q)$ for all volume fractions. The change from the fluid-crystalline to the glass phase as function of φ is clearly visible. A typical XCCA result for a sample in the partially crystalline phase ($\varphi=0.529$) is shown in Fig. 2. No single peaks are observable, instead a maximum for all l around $q=0.028$ nm^{-1}, i.e. at the maximum of $S(q)$. Therefore, we define an order parameter as $\xi(q)= <\Psi(q,l)>_l$. This is shown in Fig. 2 (top) for all samples measured. The inset shows the corresponding $S(q)$. Here, no significant

Figure 2: Ψ (q,l) for volume fraction φ =0.529.

changes are observable except the excepted q-shift for different volume fractions. The order parameter for samples in the glass phase ($\varphi \geq 0.56$) shows a small peak around $q=0.028$ nm^{-1} that increases for the crystal phase and decreases again when reaching the fluid phase. The height of the peak is shown in Fig. 3 (bottom). In addition, for the lowest volume fractions further peaks appear at higher q. As no crystallization was observed during the experiment, this observation suggest the formation of crystal precursors which will has to verified by the continuing data analysis.

[1] H. Tanaka. J. Phys.: Condens. Matter 23 284115 (2011).
[2] J. Russo and H. Tanaka. Sci. Rep. 2, 505 (2012).
[3] P.N. Pusey and W. van Megen. Nature 320, 340 (1986).
[4] E. Zaccarelli et al. Phys. Rev. Lett. 103, 135704 (2009).
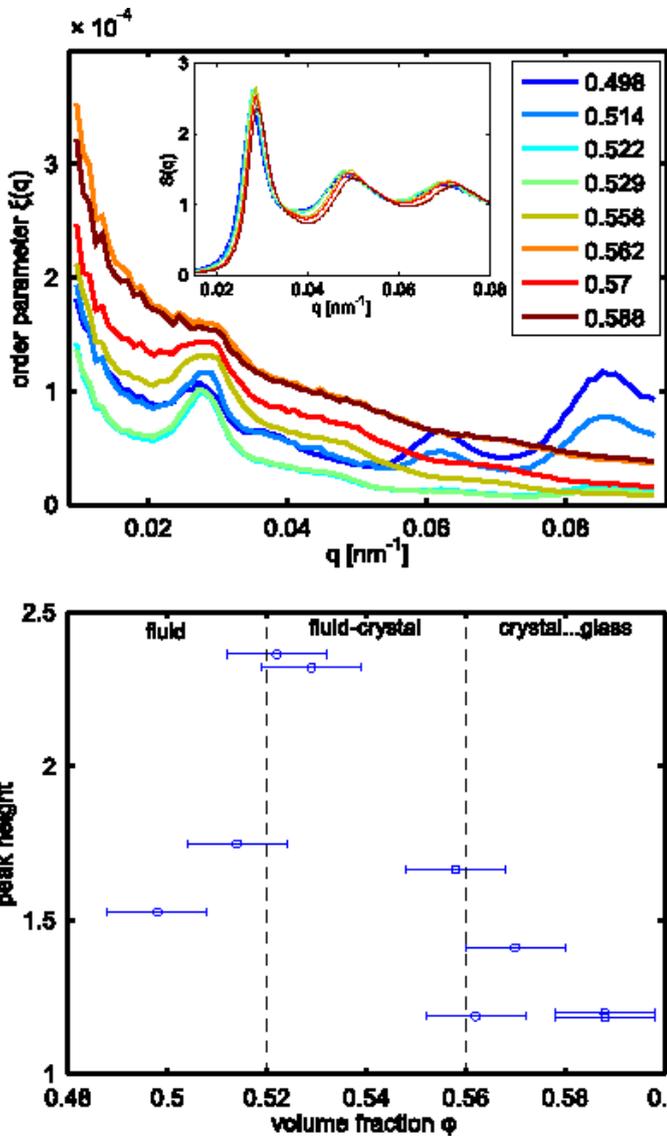[5] P. Wochner et al. Proc. Natl. Acad. Sci. 106, 11511 (2009); F. Lehmkühler et al. submitted (2013).

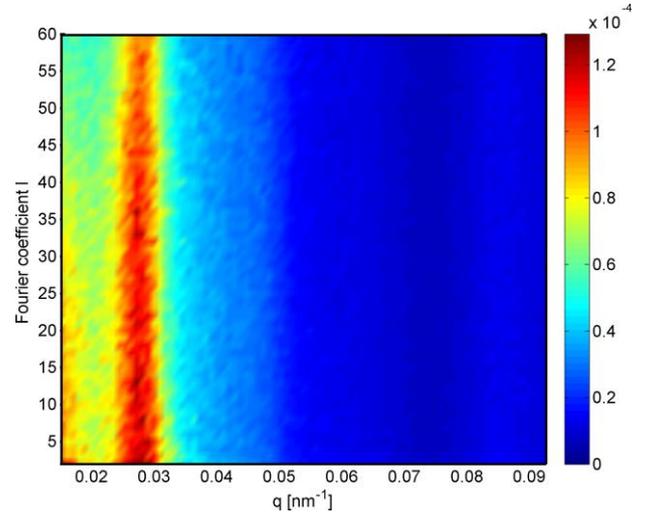*Figure 1: (top) Order parameter $\xi(q)$ for all volume fractions. The inset shows the corresponding S(q). (bottom) Relative peak height at q=0.028 nm^{-1}.*