ESRF	**Experiment title:** Crystallisation versus vitrification: role of orientational ordering in hard sphere colloids	**Experiment number**: SC-3884
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Report:

Until now it is believed, that the crystallization process is primarily controlled by positional ordering. However, molecular dynamics simulations [1] and micrsoscopy [2] studies proposed that bond orientational ordering can play a key role in crystallization. It was found that orientational bond order is observable before the onset of 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 the previous experiment SC-3531 we studied the orientational order by X-ray Cross Correlation Analysis (XCCA) in colloidal hard sphere systems at supercooled conditions and found indications for crystalline precursor structures [3]. Depending on the polydispersity in such hard sphere systems, the crystallization can be suppressed and the systems show a liquid-glass transition at high volume fractions [4]. In the framework of the experiment SC-3884 we expanded the study to such a sample system that does not exhibit a crystalline phase in order to study indications for similar higher ordered precursor clusters.

We studied PMMA spheres dissolved in decalin at volume fractions ranging from 0.49 to 0.58, a similar region that was used in the previous crystallization study. The average particle radius was 70 nm with a high polydispersity of $p = \frac{\Delta r}{\langle r \rangle} = 0.15$ avoiding crystallization. We used the standard SAXS set-up at ID10 with a sample-detector distance of about 5 m. The detector was the Maxipix 2x2 detector and an X-ray energy of 8 keV was chosen. The samples were filled into 0.7 mm thick glass capillaries that were sealed by melting the glass. The capillaries were placed in the standard sample holder at ID10. For each sample first an XPCS run was measured to determine the sample dynamics. Afterwards, speckle patterns were taken at 1000-2000 different spots on the sample, at each spot at least 10 patterns were measured to check for consistency. The patterns were analyzed according to the XCCA scheme [5]. Similar to the previous results [3], we were not able to observe single peaks in the cross correlation function $\Psi(q, l)$. Therefore, we study the symmetry averaged $\langle \Psi(q, l) \rangle_l$

as measure of higher order correlations in the sample, see Fig. 1. In contrast to the correlations found in the previous experiment at $p = 0.07$ and similar volume fractions [3], the peaks around at the next-neighbor distance are less pronounced. Furthermore, they equal the results for the disordered, glass-like samples at high volume fractions. This suggests that hard-sphere systems with suppressed crystallization do not show any higher order precursor structures, likely due to geometrical frustration because of the high polydispersity. These observations will be verified by the continuing data analysis.

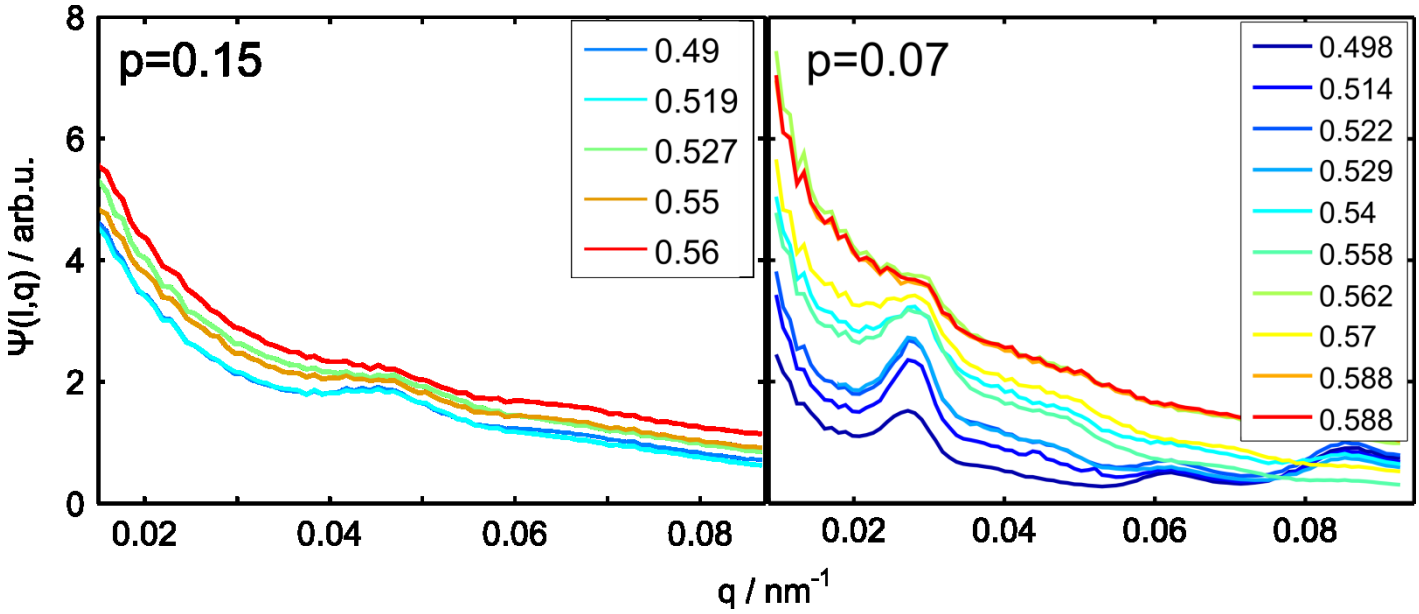

Figure 1: Symmetry averaged orientational order for p=0.15 and p=0.07 (from [3]). The corresponding volume fractions are given in the figure legends.

References

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