Investigation of the role of bond ordering on the crystallization process of hard sphere colloids with X-ray cross correlation analysis

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Until now it is believed, that the process of crystallization is primarily controlled by positional ordering, and not by bond orientational ordering. In contrast to classical nucleation theory, Tanaka et al. proposed that bond orientational ordering can play a key role in crystallization [1, 2]. Before the crystallisation sets in, an increased orientational order can be observed. In this experiment, we investigated such a change of local order in colloidal hard sphere systems via X-ray Cross Correlation Analysis (XCCA) [3, 4].

The experiment was performed at beamline P10 using the Small-Angle X-ray Scattering (SAXS) set-up with a sample-detector distance of 5 m. The detector was a Princeton Instrument CCD camera with a pixel size of $20 \mu m$. The x-ray energy was chosen to 8 keV at a beam size of $10 \times 10 \mu m^2$. As sample we used colloidal sphere of poly(methyl methacrylate) (PMMA) that are dispersed in decalin. They had a radius of $r_1 = 125.5$ nm at a polydispersities of $\Delta r_1 / r_1 = 7.1\%$ that allows the sample to crystallize [5]. We measured the sample at various volume fractions $\varphi$ between 0.5 and 0.6, thus covering the fluid, crystalline and glassy phase. First, we performed a quick X-ray Photon Correlation Spectroscopy (XPCS) run to measure the dynamics of the sample. Afterwards, we performed a long XCCA run by moving the sample to different position after a few patterns were taken. In this way we achieve different realisations of the sample. It is important to mention that we did not observe any Bragg peaks, so the samples were measured in a metastable, ”supercooled” state. To identify the degree of orientational order, we calculate the correlation function [4]

$$\Psi(l, q) = \text{var}(I_l(q) / \langle I(q) \rangle_\omega),$$

(1)

where $I_l(q)$ is the $l$th Fourier coefficient of the intensity $I(q)$ with respect to the azimuth angle $\omega$ of the two dimensional scattering pattern. This is shown in Fig. 1 for two selected volume fractions.

![Figure 1: Orientational order $\Psi(l, q)$ of two selected samples.](image_url)

While the glass-like sample ($\varphi = 0.588$) shows a monotonical decrease of $\Psi$ with $q$, the sample in the fluid-crystal coexistence phase exhibits a maximum around the maximum of $S(q)$ around $q_{max} \approx 0.28$ nm$^{-1}$. Most importantly, in contrast to computational work, $\Psi$ does not vary significantly with
Therefore we define an order parameter \( \xi(q) = \langle \Psi(l, q) \rangle \). In general, \( \xi \) is found to increase with \( \varphi \). In addition, the peak around \( q_{\text{max}} \) for the low volume fractions is well reflected, see Fig. 2. We interprete the relative increase of orientational order at \( q_{\text{max}} \) accompanied by further maxima at larger \( q \) as indications of crystalline precursors that are in line with the observations from Refs. [1, 2] and cannot be observed in the glass phase. Further data analysis and interpretation is in progress.

![Figure 2: Order parameter \( \xi(q) \) for selected volume fractions as indicated.](image)

**References**