Detecting order in the disorder- local symmetries in hard colloidal glasses

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Disordered materials, such as glasses and liquids, do not exhibit translational symmetry and are thus able to accommodate different local symmetries in one and the same system. Among those symmetries is the icosahedral order which can not fill space periodically and is held responsible for the undercooling of liquids and the glassy state [1-3]. The local symmetries are not accessible in conventional X-ray diffraction experiments as the time and ensemble averaging process yields an average structure factor \( <S(Q)> \) which carries no information about local bond order. This limitation can be overcome by performing coherent X-ray scattering experiment. This is illustrated by a study of slow supercooled liquids and glasses. A coherent X-ray beam scattered from a quasistatic disordered sample produces a speckle pattern which reflects the exact spatial arrangement of the particles. That is the speckle pattern contains information about the local structure of the sample and appropriate correlation functions have to be defined to extract this information.

We measured coherent SAXS patterns of hard spheres colloidal glasses out of PMMA dispersed in decalin with radii varying between 70 to 130 nm, different polydispersities and volume fractions. The samples were prepared as described in [4]. The resulting structure factor and CCD image of a hard sphere system with a radius of about 127 nm, polydispersity of about 6.6 % and volume fraction \( \phi = 0.52 \) are shown in figure 1. At \( \phi = 0.52 \) the particles are partially crystallized, which is visible via Bragg peaks appearing in the CCD image and in the structure factor.

![Figure 1: a) Structure factor S(q) (left) and CCD (right) of the hard sphere colloidal particles.](image)

In contrast to incoherent diffraction the scattering of coherent X-rays gives access of the instantaneous positions of all the atoms/particles in a particular sample in reciprocal space. In this case the resulting speckle pattern reflects the exact spatial arrangement of all particles in the beam and one can thus attempt to extract information on the local order [5]. To uncover the hidden local bond order in disordered matter from the speckle pattern a higher order correlation functions have been defined:

\[
L(i,q,l) = \Re \left( \int_0^{2\pi} d\phi e^{i\phi} I(q,i,\phi) \right)
\]

(1)

The Fourier component of the common building block can be extracted from a set of speckle patterns by calculating the variance, i.e. the fluctuations of the relevant symmetries expressed by
\[ \Psi_L(q,l) = \langle L(i,q,l)^2 \rangle - \langle L(i,q,l) \rangle^2 \]

which represents the fluctuations of the Fourier component \( l \) of the cross correlation function. As an example we show here the variance of the hard sphere colloidal system (Figure 2).

Figure 2: (left) Variance \( \Psi_L(q,l) \) for the volume fraction \( \phi = 0.52 \) of the hard sphere colloidal system. (right) Autocorrelation function of the fluctuation of the symmetry for the Fourier components \( l = 2, 6, 10 \) and 12.

It can be clearly seen, that the variances for the different Fourier components differ and especially the Fourier components \( l = 6 \) and \( l = 14 \) are more pronounced (figure 2 left) than the others. It is also possible to monitor the fluctuations as a function of time yielding insight in the relaxation of the different Fourier components as shown in Figure 2 (right).

In our experiment performed at the PETRA P10 beamline we investigated seven different hard sphere systems at high volume fractions. The XCCA method allows to study the bond order and thus the local structure of colloidal glasses. In particular, the shape of the structure factor already indicates local bond order. By comparing the experimental data for the different hard spheres system with results of MD simulations we want to learn more about the details of the local bond order of hard sphere systems.

References