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Report:

Colloidal suspensions are intensively studied by theory, experiment and computer simulations. As most studies focus on idealized systems, only a small subset of the large experimentally accessible parameter space is covered. In particular, the present knowledge regarding effects of particle size- and charge-polydispersity is rather limited. The focus of the performed experiment was thus to gather data on the effect of polydispersity on the interparticle structure and short-time diffusion.

To access the hydrodynamic functions of polydisperse suspensions, measurements of the sample structure and dynamics are needed. This has been achieved by using partially coherent X-rays in small angle X-ray scattering (SAXS) geometry, whichs covers the required momentum transfer range. In the experiments, the temporal fluctuations of the scattered intensity allowed to extract the sample dynamics from intensity autocorrelations (X-ray photon correlation spectroscopy), while the time average of the SAXS patterns gives access to the intra- and interparticle structure on typical length scales of mesoscopic colloidal systems.

The measurements were performed in SAXS geometry, at a photon energy of 21 keV. The beamsize on the sample was set to around 10 x 10 μm^2. Two detectors, placed approximately 5 m behind the sample, were used: A Cyberstar Scintillation detector, directly connected to a hardware autocorrelator to allow for the direct computation of autocorrelation functions and a Maxipix 3x1 area detector, equipped with a 500 µm thick CdTe sensor bump-bonded to three Medipix chips in a 3 x 1 layout.

The sample system was a bimodal mixture of two unimodal stock solutions. Both stock solutions consisted of spherical nano-particles with a size polydispersity of around 7±1 % in case of both systems. The mean radii were 37 nm and 55 nm, respectively. These stock solutions were mixed at 3 different particle number ratios, 2 total volume fractions and 2-3 different salt concentrations screening the direct particle interactions, resulting in a total of 15 bimodal sample systems which were measured during the beamtime.

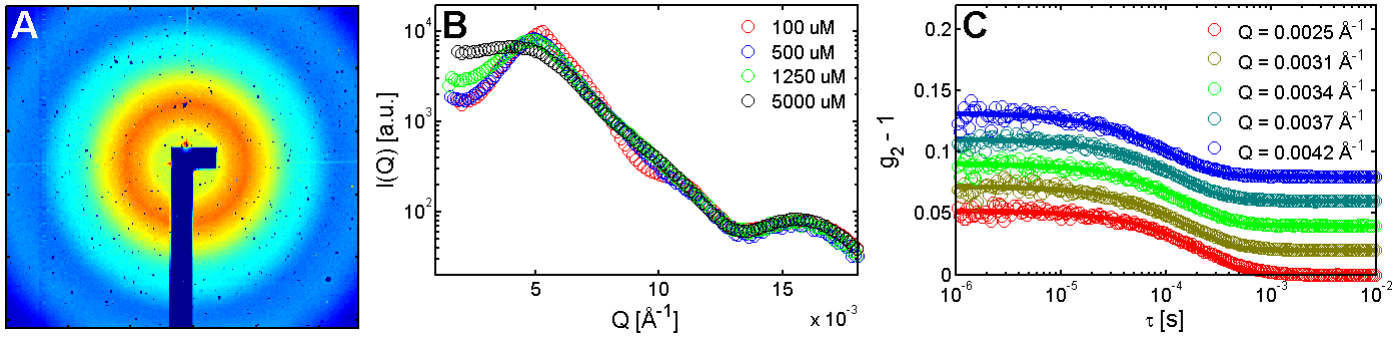

Fig.1 A: Example scattering pattern recorded with the Maxipix 3x1 for a bimodal sample at an electrolyte concentration of 100 µM. B: Azimuthal integrated scattering intensities of a set of 4 samples with different salt concentrations and otherwise unchanged sample parameters. C: Autocorrelation functions of a bimodal sample. The symbols display the measured g_2–functions, the solid lines are fits. The autocorrelation functions have been offset vertically for better visibility.

Figure 1A shows the sum of a series of 4000 scattering patterns (exposure time of 0.01 s per frame). The first minima of the particle form factor P(Q) are resolved even for the smaller particle species, as can be appreciated by the rings of undulating intensity. As the individual particles of this sample are interacting, a ring of high intensity is visible close to the center of the pattern which is due to the static structure factor S(Q) modulating the scattering intensity I(Q). The corresponding azimuthal integrated scattering intensity is displayed in figure 1B, together with three different samples where only the electrolyte concentration was changed while all other sample parameters were kept constant. While the I(Q) of the four samples look almost identical for $Q > 0.013$ Å^{-1}, distinct differences can be seen around $Q = 0.005$ Å^{-1} where the first maximum of the static structure factor is located. Here, the peak height decreases with increasing electrolyte concentration, a sign of the stronger screening of the direct particle interactions.

Due to the fluid nature of the samples, the dynamics are purely diffusive and were thus recorded using the employed Cyberstar point detector which is able to measure events with a frequency of 100 kHz and above. At a given point in reciprocal space, the scattering signal was recorded for 600 s and the corresponding intensity autocorrelation function $g_2(Q, \tau)$ was calculated. Example autocorrelation functions are displayed in figure 1C. As a first approximation to the data, solid lines display the result of a single exponential decay to the data. As expected, the typical relaxation times of the autocorrelation functions shift towards shorter times with increasing Q-value.

Data evaluation is currently ongoing. Part of the applicants have developed a set of accurate analytical-theoretical schemes [1-4] and computer simulation techniques [1,4,5] for the fluid microstructure and short-time diffusion in suspensions of charged colloidal spheres. This methods feature accurate inclusion of colloidal charge regulation [2,3] and the intricate solvent-mediated hydrodynamic interactions [1,4,5] in theory and simulation. The most recent theoretical and computer simulation work accounts for pronounced particle polydispersity in calculating the hydrodynamic interactions [4,5]. The results of the beamtime will thus serve as an accurate and profound test of the developed theoretical framework.

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