ESRF	Experiment title: Systematic study of the dynamic behavior of charge-stabilized colloidal suspensions with reversibly screenable particle interactions	Experiment number: SC2552
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Report:

In colloidal suspensions, direct particle interactions, like electrostatic or steric repulsion are introduced to avoid agglomeration due to the attractive van-der-Waals force. In addition to these interactions, indirect, hydrodynamic interactions mediated by the solvent play an important role for the dynamic behavior of these systems. However, while the hydrodynamic interactions in the case of steric stabilized colloids are well

understood and explained both by therory and experiment, the publications of the last decade [1-5] reveal evident discrepancies between experiments and existing theories of the more complex electrostatically stabilized systems.

Therefore we studied the direct and indirect particle interactions of a novel charge-stabilized system – synthesized via а copolymerisation of a fluoro- and a silyl-methacrylate. To avoid beam damage of the sample system, the experiments were carried out in a flow through set-up, allowing thus to reduce the time for the samples to be exposed to the collimated beam. This flowthrough set-up consists of a quartz glass capillary attached to a flexible, circulatory tube system including a pump device as shown in fig. 1. A switching mechanism for salt injection give the possibility to add a defined amount of electrolyte to screen the direct particle interactions in the suspension, being thus able to change the direct particle interactions without changing the volume fraction Φ of the sample.

The sample system investigated consisted of charge-stabilized colloids having a mean particle diameter of 112 nm. The volume



Fig. 1: Flow system with the flowthrough glass capillary attached to a pumping system.

fractions investigated ranged from $\Phi = 0.3$ to $\Phi = 0.08$, while the added electrolyte concentration was varied between 0 μ M and 150. mM potassium chloride. For all of these samples static and dynamic scattering experiments were performed, using either Small Angle X-ray Scattering (SAXS) or X-ray Photon Correlation Spectroscopy (XPCS). In a static scattering experiment, the measured intensity I(Q) is given by I(Q) =

S(Q)/P(Q) were S(Q) is the static structure factor and P(Q) is the particle form-factor. Measuring a completly screened sample showing no direct particle interactions (S(Q) = 1), the particle formfactor was obtained. For the samples showing direct particle interactions the static structure factor was extracted by dividing the measured intensity by the particle form factor.

The extracted static structure factors for three samples (A: $\Phi = 0.3$, 1000 μ M KCl, B: $\Phi = 0.3$, 3500 μ M KCl and C: $\Phi = 0.3$, 35.000 μ M KCl) are shown in fig. 2. The static structure factors described by rescaled mean spherical approximation [6] yielding an average charge of 780 e⁻ per colloidal particle.

То study the dynamics of the system, autocorrelation functions were measured at different momentum transfers using a scintillation detector. From these autocorrelation functions the dynamic structure factor $D_0/D(Q)$ was extracted hydrodynamic and the functions $H(Q) = [S(Q) \times D(Q)] / D_0$ were calculated.

Fig. 3 shows the hydrodynamic functions for three samples (A: $\Phi = 0.08$, 0 µM KCl, B: $\Phi = 0.15$, 0 μ M KCl and C: $\Phi = 0.3$, 1000 μ M KCl). These hydrodynamic functions show an extreme slowing down of the system especially for concentrated colloidal suspensions, which is currently not supported by any theoretical model. Even the recently developed accelerated stokesian dynamics model [5] cannot explain the dramatic slowing down of the particles' mobility which we observe in our model system. The analysis of this effect is still ongoing - the measured hydrodynamic functions are currently compared with previous results and theoretical models.

References

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Fig. 2: Static structure factors and corresponding RMSA-fits for three samples of the same volume fraction $\Phi = 0.3$ and three different salt concentrations.



Fig. 3: Hydrodynamic functions of three investigated samples.