



Experiment title:
 Static and dynamic behaviour of electrostatically stabilized colloidal systems in the moderate concentration range using a flow-through cell

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 SC-2826

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Report:

Colloidal systems, which can be seen as model systems for condensed matter, are of great interest for applied as well as for fundamental research. These colloidal nano-particles have to be stabilized to avoid agglomeration by the attractive Van-der-Waals force. Colloidal systems can be distinguished by the stabilization of the particles and can be divided into ‘hard sphere’ and ‘soft sphere’ systems. Hard sphere colloidal particles are sterically stabilized by a polymer coating resulting in a short-range interaction potential, whereas soft sphere colloidal particles are stabilized by charged surface groups. These latter ones can be considered as “macro-ions” and interact via a long-range, screened Coulomb potential: $V(r) = e^2 z^2 (4\pi\epsilon_0\epsilon_r)^{-1} \exp(\kappa r)$ where z is the effective number of charges per colloid, ϵ_0 is the vacuum dielectric constant and ϵ_r the relative dielectric permittivity of the solvent and r is the inter-particle distance. κ is the inverse Debye screening length with $\kappa = e^2 (k_B T \epsilon_0 \epsilon_r)^{-1} (nz + 2c_s)$, where n is the number density of the macro-ions and c_s is the amount of added electrolyte. Changing of the direct interaction strength is therefore possible by either varying the concentration of electrolyte or by changing the particle volume fraction Φ .

These soft-sphere systems start to order already at low volume fractions compared to hard sphere systems and their static behaviour can be described by the rescaled mean spherical approximation [1]. The aim of our experiment was to analyse the indirect, hydrodynamic interactions of these particles which are mediated by the solvent. As the hydrodynamic interactions $H(Q)$ depend both on structure and the dynamic behaviour of the systems, they are accessible by measuring both the static and the dynamic structure factor and can be extracted via the relationship $H(Q) = S(Q) / (D_0/D(Q))$.

For the hydrodynamic interactions the experimental results can be grouped into three different concentration ranges. In the case of very dilute colloidal suspensions (volume fraction $\phi < 0.008$) the experimental results show an increase of the mobility of the colloids due to the hydrodynamic interaction ($H(Q_{max}) > 1$) [2], whereas in the case of concentrated suspensions ($\phi > 0.1$) the experimental results indicate a slowing down of the system ($H(Q_{max}) < 1$) which resembles the hard-sphere case [3] or can be even dramatically slower [4]. In our experiment we had a look at the region of moderately concentrated charge stabilized colloidal systems ($0.008 < \phi < 0.1$).

To avoid beam damage of the sample, 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 flow-through set-up consisted of a quartz capillary attached to a tube system connected to a syringe pump to allow for a steady flow also at low pumping speeds. The flowing velocity inside the capillary was set such that the colloidal particles were 1 – 3 seconds exposed in the X-ray beam which was collimated to $10 \times 10 \mu\text{m}^2$ and the photon flux on the sample was 2×10^{10} photons/sec@100mA. The use of the same flow-through capillary allowed the exact measurement and subtraction of the scattering arising from the solvent and the capillary itself to achieve data of high quality.

The sample system investigated consisted of charge-stabilized colloidal particles having a mean particle diameter of 90 nm. The volume fractions investigated ranged from $\Phi = 0.02$ to $\Phi = 0.04$. 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 $I(Q) = S(Q)/P(Q)$ where $S(Q)$ is the static structure factor and $P(Q)$ is the particle form-factor. Measuring a completely screened sample showing no direct particle interactions ($S(Q) = 1$), the particle form-factor 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. To study the dynamics of the system, autocorrelation functions were measured at different momentum transfers using a avalanche photo detector. From these autocorrelation functions the dynamic structure factor $D_0/D(Q)$ was extracted.

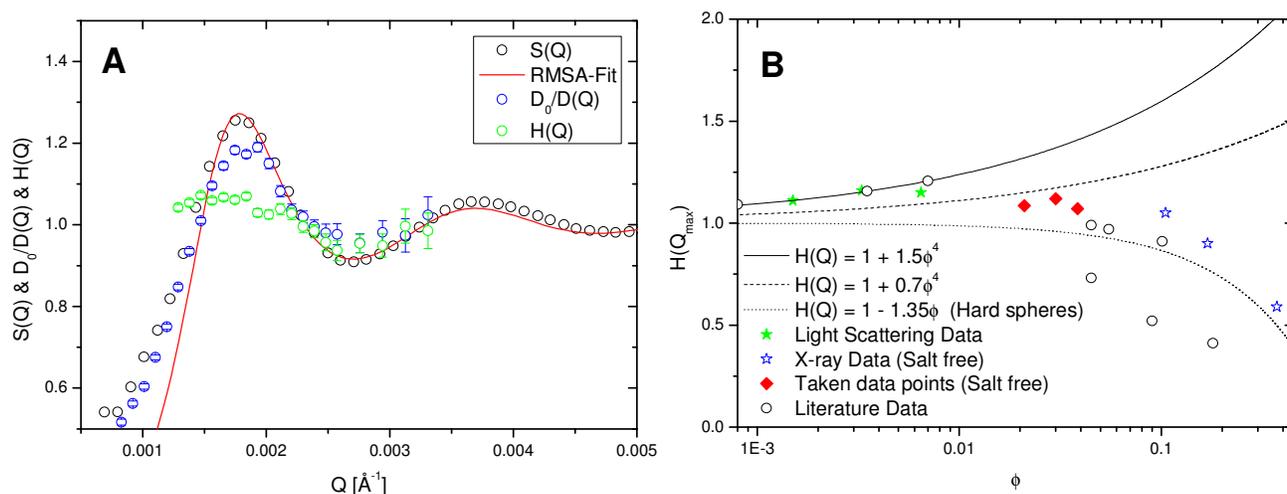


Fig. 1:A: Static structure factor $S(Q)$, dynamic structure factor $D_0/D(Q)$, hydrodynamic function $H(Q)$ and RMSA-Fit to the static structure factor for a sample measured. B: Maximum of the hydrodynamic function depending on the volume fraction ϕ . The blue stars indicate X-ray data taken during a previous experiment (SC 2325), the green stars indicate data taken using dynamic light scattering, the black circles show data from literature [2-4]. The red diamonds show data taken at this experiment. All data points shown are samples where no additional salt was added.

In figure 1A the static and dynamic structure factor and the resulting hydrodynamic function of one of the samples measured is shown. In figure 1B the maximum of the hydrodynamic function $H(Q_{\text{max}})$ of three salt free samples in comparison to former experiments and literature data is shown, which are gapping the region of the pairwise-additive behaviour of diluted systems and the more hard-sphere like behaviour of concentrated systems. The analysis of data is still ongoing – the measured hydrodynamic functions are currently compared with theoretical models.

References

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