ESRF	**Experiment title:** Effect of confinement on dynamics of colloids	**Experiment number**: SI-612
Beamline: ID10A	**Date of experiment**: from: 12 Feb. 2001 to: 19 Feb. 2001	**Date of report**: 28 February 2001
Shifts: 18	**Local contact(s)**: F. Zontone	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

J.F. van der Veen[1)]*, J.H.H. Bongaerts[2)]*, J. Miguel[2)]*, U. Flechsig[1)]*

1) Paul Scherrer Institut, Villigen - Switzerland.

2) Van der Waals-Zeeman Instituut, University of Amsterdam - The Netherlands.

Report:

We have performed x-ray photon correlation spectroscopy (XPCS) experiments on colloidal particles which are confined within a planar x-ray waveguide [1,2]. This is a continuation of earlier experiments we have performed at ESRF (see report of experiment SI-611). In these experiments, we observed for confined colloids a long-time non-exponential decay of the time correlation function <I(0)I(t)>. We wanted to reproduce these exciting results and perform control experiments.

Monodisperse silica spheres of 210 nm diameter were disssolved in a water-glycerol mixture having a viscosity of 3 cP. The suspension, having a volume concentration of 7 %, is confined between two flat silica surfaces which form the boundaries of the x-ray waveguide. The length of the waveguide is 5 mm. We selected an energy of 13.2 keV with a Si(111) monochromator. A transversely coherent beam was selected by a 8 micron pinhole. The scattering vector in all experiments below is in the plane of the confining surfaces (see Fig. 1).

At a gap of 2.5 microns, we again observed long-time tails in the correlation functions at small momentum transfer. We checked whether these tails were indeed caused by the confinement by changing the path length through the waveguide. This was done by translating the waveguide perpendicular to the beam (see Fig. 1). In this way the path length through the waveguide relative to that in the collar (almost 1 mm wide) around the confiment area is changed. We found that the long time tail disappeared as we moved further away from the center of the waveguide (see Fig. 1, correlation functions not shown here). This is proof that the long-time tail is caused by the waveguide. Together with the fact that the long time tail is q-dependent, this is strong evidence that we are not looking at an experimental artefact.

Figure 2 shows correlation functions measured at a single in-plane momentum transfer ($q_{//} = 4.65\ 10^{-3}\ nm^{-1}$), but for three different gap settings. As the gap is decreased, the correlation functions decrease slower and deviate more from a single exponential decay. Hence, we see a clear effect of confinement on the mobility of particles in the plane of the surfaces.

In Fig. 3 are shown the inverse time constants, obtained by fitting a single exponential decay to the first part of the correlation functions, plotted against $q_{//}^2$. The particles slow down, as the gap is decreased. It should be noted that the time constants plotted in Fig. 3 are only a first indication of what is happening to the particle diffusion. In a further analysis, the contribution of the bulky collar to the correlation function will be subtracted, and a fit will be made to remaining correlation functions.
We have shown that the diffusion of the colloids is hindered by the confinement. Hydrodynamic effects as well as structural changes within the confining space may play a role. Analysis is in progress.

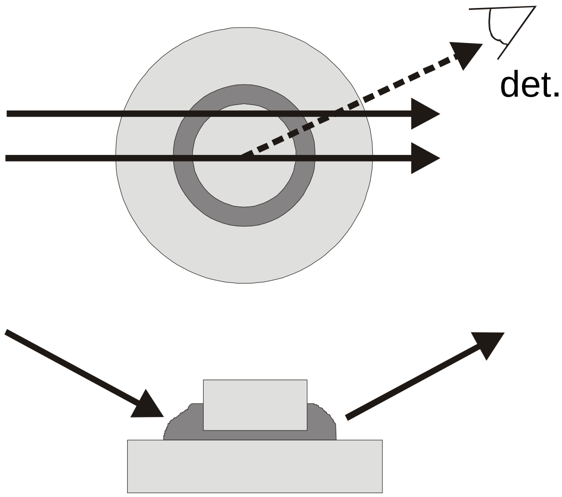


Fig. 1 Top view (top) and side view (bottom) of the scattering geometry. The dark area represents the fluid. The fluid forms a collar around the confined area. This results in a superposition of the scattering from the confined fluid with that from the bulk fluid. The total length through the fluid with collar is ca. 6.5 mm, while the maximum waveguide length is 5 mm.

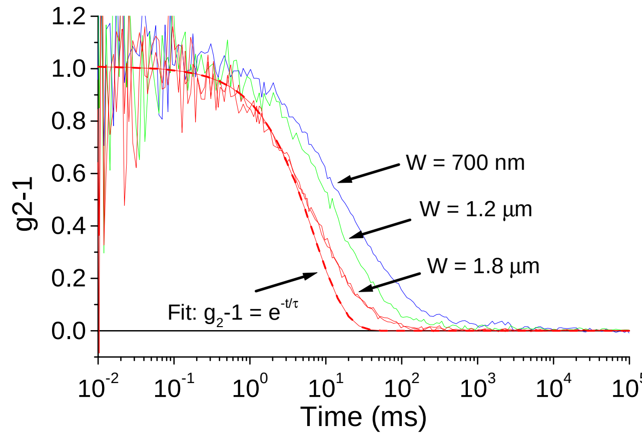
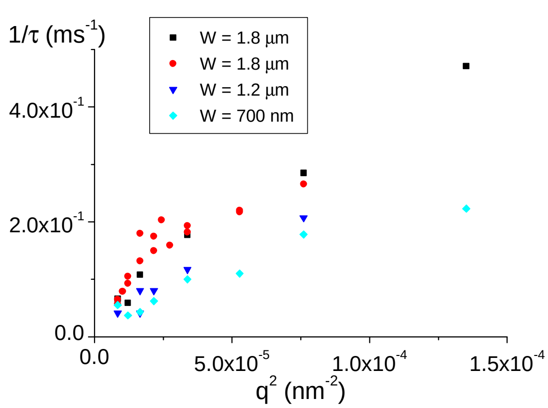


Fig. 2 Time correlation functions g_2-1 for different gap settings *W*, measured at $q_{//}$ = 4.65 10^{-3} nm^{-1}. The dynamic speckle contrast was typically 40%. For comparison, the correlation functions have been normalized to one.
As the gap is closed, the correlation function decays slower. At the smallest gap of 700 nm width, the decay time is a factor 3 longer than at a gap of 1.3 micron width. For a bulk fluid, the correlation functions can be fitted to a single exponential decay. With the functions shown here, this is not possible. A single exponential fit was made to the first part of the *W*=1.8 μm correlation function in order to demonstrate the deviation.



← ← **Fig. 3** Inverse decay-time constants as fitted to the first part of the correlation function (see the fit in Fig. 2). As the gap is decreased, the particles move slower, which is indicated by the slower decay of the correlation functions. Furthermore, the deviation from the single exponential decay (expected for bulk single particle diffusion) is increased at smaller gaps.

References:

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[2] M.J. Zwanenburg, J.F. Peters, J.H.H. Bongaerts, S.A. de Vries, D. L. Abernathy, and J. F. van der Veen, Phys. Rev. Lett. 82 pp. 1696 (1999).