Coherent light and x-ray scattering studies of the dynamics of colloids in confinement
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Summary

The aim of this thesis is to reveal the dynamic properties of ultrathin fluids, confined in between two closely placed flat solid surfaces. The work is motivated by the observation that a fluid confined in a gap of less than a few times the diameter of the fluid’s building blocks shows confinement-induced freezing, resulting in an enhanced viscosity and elasticity of the fluid. This affects the lubricating properties of fluids confined between two sliding objects, but also other circumstances in which a fluid is confined within a narrow space.

The method we employ for investigating ultrathin confined fluids is the x-ray waveguide technique. Consider a fluid confined in between two flat silica disks, which have a diameter of several millimeters. Piezo-driven motors position the disks opposite to each other and the gap in between the disks, in which the fluid resides, can be set between ca 20 nm and several micrometers. For x-ray wavelengths the refractive index of fluids is generally higher than that of the solid walls, which enables the fluid layer to serve as the guiding layer for x rays in a waveguide geometry. If the angle between the propagation direction and the walls is below the critical angle for total reflection at the fluid-wall interface, the x rays are internally reflected and are thus confined to the fluid layer. The propagation of the x rays within the waveguide is described in terms of so-called waveguide modes. Because almost all intensity propagates within the fluid and not within the walls, the signal-to-noise ratio of the x-ray waveguide technique compares favorably to that in standard reflectivity or transmission experiments, where the x-rays travel through the thick confining walls before reaching the small scattering volume of the fluid. If the confined fluid is ordered or if it contains macroscopic (colloidal) particles this will result in scattering between the waveguide modes. By analyzing the time-dependent far-field diffraction patterns behind the exit of the waveguide, we obtain the structural and dynamical properties of the confined fluid. The principles of the x-ray waveguide technique are described in chapter 2.

In order to perform experiments on the smallest possible gap sizes we made two important technical innovations, which we present in chapters 3 and 4. The separation and parallelism between the two disks is monitored by an optical interferometer technique called fringes of equal chromatic order. For this purpose the surfaces are coated on the side of the guiding layer by semi-transparent aluminum mirrors, which together form the cavity of the optical interferometer. The minimum separation between the mirrors that can be measured in this way is half an optical wavelength (~ 250 nm), much larger than the minimum gap for the x-ray waveguide (~ 20 nm). In chapter 3 we describe how we overcome this limitation by depositing a silica spacer layer on top of the aluminum layer, resulting
in a multistep-index-waveguide geometry. In this manner we spatially separate the optical mirrors from the waveguide surfaces. We have observed “cladding” modes travelling within the spacer layers and we give a full explanation of their behavior. Using the multistep-index geometry, we have observed an unperturbed propagation of the x rays through an empty waveguide with a length of 4.85 mm and a gap of 59 nm. Smaller separations are feasible.

Both the scattering volume of a thin fluid and the refractive-index contrasts for x rays are very small. Hence, the scattered intensities may be too low in an x-ray waveguide experiment, even if we use an x-ray source as bright as the European Synchrotron Radiation Facility. In chapter 4 we demonstrate how we obtain a coherent flux enhancement within the waveguide by almost two orders of magnitude by pre-focusing an x-ray beam of 200-micrometer height in one dimension into a 1-micrometer high line focus at the entrance of the waveguide. The flux enhancement enables x-ray waveguide experiments at smaller gaps and lower refractive-index contrasts. The focusing device is a linear diffractive lens (a Fresnel zone plate) operating in transmission. The lens affects the transverse coherence length of the beam at the entrance of the waveguide, which is important for coherent scattering experiments. In the absence of the lens the transverse coherence length along the confining direction is \( \sim 100 \) micrometer in our configuration, in the presence of the lens it is equal to the spatial resolution of the imaging system in the image plane, which is \( \sim 0.3 \) micrometer. We describe the propagation of the partially coherent x-ray beam from the source, via the lens and the waveguide to the detector plane in terms of the mutual intensity function. The observed diffraction patterns are reproduced by numerical beam-propagation calculations, where partial coherence of the beam is taken into account via the mutual intensity function. The results presented in chapter 4 enable us to define the optimum conditions for enhancing the flux within the waveguide, while matching the transverse coherence length of the beam to the size of the gap between the confining plates.

Before investigating the dynamics of confined colloidal suspensions, we consider in chapter 5 the long-term dynamics of bulk colloidal suspensions consisting of charged silica spheres with a radius of 54.9 nm. Initially, these experiments were intended as a reference for the confined colloidal suspensions, but these charged-stabilized colloids actually are an intriguing object of study by themselves, showing complicated visco-elastic behavior such as shear thinning and glass and gel formation. Most colloidal suspensions strongly scatter light of visible wavelengths, due to large refractive-index contrasts between the solvent and the colloidal particles. This frustrates experiments using standard light scattering techniques. By using the techniques of dynamic x-ray scattering and cross-correlated dynamic light scattering, we overcome this problem and we are able to observe the dynamical
properties of strongly scattering fluids. We studied fluid systems with varying colloidal volume fraction and varying Debye screening length. The colloidal dynamics can be explained qualitatively by the cage effect. At short times the particles diffuse within their cages, formed by their surrounding neighbors. At longer times the particles reach their cage boundaries and the diffusion process slows down until at the longest times the cages break up and long-time diffusion sets in. We found that the relaxation of the diffusion function can be scaled onto one single master curve for all suspensions in the liquid phase. This master curve has an algebraic long-time tail, as is predicted by theoretical calculations. Furthermore, we observed that one of the colloidal suspensions was a stable supercooled colloidal fluid. It did not show aging in the course of the experiments, but finally solidified after several years. This is the first observation of a truly supercooled colloidal fluid. The question whether the solidified system is a reversible gel or a glass could not be answered due to the long time scales involved in the solidification process. Based on the results of chapter 5 we suggest experiments on charge-stabilized colloidal suspensions close to the liquid-solid phase transition. By performing rheological measurements of the fluid’s visco-elastic properties and simultaneously performing in-situ cross-correlated dynamic light scattering measurements, it will be possible to directly test the validity of the generalized Stokes-Einstein relation, which relates the particle diffusion to the fluid’s viscosity.

In chapter 6 we discuss the dynamic properties of a dilute colloidal suspension confined in between two flat plates. The suspensions consist of lightly charged silica spheres with a radius of 115 nm and they form the guiding layer of an x-ray waveguide. We work out the theory for dynamic x-ray scattering in the waveguide geometry, which is more complicated than scattering from a bulk sample. The latter relates to the fact that the x rays propagate as standing waves in the confining direction, not as plane waves. We observed that the short-time diffusion coefficient of the spheres within the plane of the waveguide is enhanced when compared to the same suspension in bulk. However, when the gap is decreased further, the diffusion slows down again. At longer times the diffusion is sub-diffusive (fractal Brownian motion), as evidenced by long algebraic tails in the time-dependent mean-square displacement. We believe that this is caused by an inhomogeneous distribution of surface charges on the confining walls. This results in a position-dependent particle-wall interaction, which hinders particle diffusion. The effect of the inhomogeneities of the surface charges can be further investigated by purposely modifying the distribution of the surface charges.

In the future, the experiments on confined fluids will be combined with surface force measurements. An experimental setup that combines x-ray diffraction experiments on confined nanometer-thin fluids with surface force measurements has
been constructed. Such comparisons will make it possible to relate the macroscopic forces to the microscopic structure and dynamics.