The phase behavior of a weakly attractive colloidal system
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In this thesis, we investigate the colloidal phase behavior in a weakly-attractive system. To this end, we employ dynamic light scattering, small-angle X-ray scattering and confocal microscopy to quantitatively characterize the different phases formed. The result is a colloidal phase diagram with gas, liquid and crystalline phases.

The experimental system consists mainly of charge-stabilized polystyrene or fluororinated spheres suspended in a mixture of 3-methylpyridine, water and heavy water. The choice of this particular system is made because density matching - for polystyrene - or index matching - for the fluorinated spheres - between particle and suspending liquid is possible. Furthermore, the pyridine/water system exhibits a closed loop in the $T$-$x$ phase diagram with an upper and lower consolute point. The lower consolute point lies in the convenient range of 30 to 70 degrees centigrade. The closed loop can be shifted, enlarged and shrunk by changing the ratio of water to heavy water and the addition of salt. Thus we can control the repulsive interactions, the Van der Waals potential and the gravitational field to study the effect of the specific attractive interactions when the two-phase region of the suspending liquid is approached: the solvent mediated interaction or the critical Casimir effect. The existence of this attractive interaction was pointed out by Fisher and de Gennes, its practical consequences Beysens and coworkers. They observed the reversible aggregation of silica particles in a binary mixture of lutidine and water approaching its bulk-phase coexistence temperature. Charge-stabilized colloidal particles in binary mixtures have a unique feature that sets them apart from other systems. The temperature can be used as external and continuous parameter to control the amplitude and range of the attractive force. Thus, temperature offers a convenient means to study the phase behavior of the colloidal system by external control. In this thesis we show that the aggregation observed by Beysens is in reality a reversible phase transition in the colloidal system. Density matching between the particles and the suspending medium enabled us to observe for the first time to observe stable gas-liquid,gas-solid.
and liquid-solid equilibria. In a density matched system the nuclei of the next phase can, in principle, grow to macroscopic dimensions, while in a non-density-matched system gravity perturbs this growth process at a very early stage.

In chapter two, we describe three experimental techniques used in our study of the colloidal phase behavior in real, and q-vector space. The characterization of particles and binary mixtures is treated in detail.

In chapter three we use the mean field model, proposed by Fisher and de Gennes, to describe the interaction between the particles. In a calculation for the fluorinated particles we can consider the Van der Waals force negligible, because the refractive index of the particles is close to that of the solvent. Then only two contributions remain for the interaction, one is the attractive critical Casimir interaction governed by the correlation length of the binary mixture, the other is the repulsive screened Coulomb interaction with a range determined by the Debye screening length. The two length scales in the problem, the correlation length and Debye screening length can be determined from the properties of the suspending binary liquid. The phase diagram of the binary liquid sets the calibration and forms the matchsticks of the length scales. With these length scales as input we obtain values for the condensation temperature $T_a$ that agree well with the observations. We concluded that the critical Casimir effect is the dominant mechanism of attractive interaction in this colloidal system.

In chapter four, we demonstrate how to determine the two characteristic temperatures $T_{cx}$ and $T_a$ by turbidity measurement and visual observation. We use small angle X-ray scattering to characterize these phases as colloidal gas, liquid, fcc crystal and glass. The phase behavior that we observe with SAXS, turbidity measurement and visual observation is summarized in a phase diagram for the colloidal system, where we plot $\Delta T = T_{cx} - T_a$ versus the volume fraction $\phi$ in Fig.7.11.

From all the data obtained for colloids in a binary liquid mixture, it is clear that this temperature difference is the experimentally relevant parameter to describe the state of the colloidal system. At low volume fraction, the colloidal system shows two stable phases: fluid and crystal. At higher volume fraction, we observe equilibria of gas and liquid, and liquid and solid. The similarity of the diagram we obtain in the experiment with the diagrams suggested by Frenkel for attractive colloidal systems is striking. The existence of a gas-liquid coexistence region before the liquid-solid coexistence suggests that there is a long-range attractive potential. The density match between particle and solvent is essential to study the colloidal phase behavior in a binary mixture. A small density difference disturbs the growth of the nuclei in a very early stage. Only under microgravity the true nature of the colloidal phase...
In chapter five, we investigate the colloidal phase behavior by microscope. Polystyrene spheres, silica particles, and fluorinated particles are used to perform the measurements. The observations on the systems with polystyrene and silica spheres are consistent with the results from the SAXS measurements. The fluorinated particles show similar, but in two aspects different behavior. Firstly, the condensation occurs on the pyridine-rich side of phase diagram. This indicates that the fluorinated particles prefer a water-rich adsorption layer as opposed to the polystyrene particles which prefer a pyridine-rich adsorption layer. Hence the condensation takes place on the water-rich side of phase diagram. Secondly, the structure of the condensed phase is characterized as gel or glass-like structure as opposed to the crystal structure we observe for the systems with polystyrene and silica particles. Nevertheless, the transition remains reversible. In this refractive index matched system the only remaining attractive interaction is the critical Casimir effect. The difference in observed structures the system condenses into may be due to gravity.

In chapter six, the dynamics of crystallization is studied by means of SAXS measurements. We observed two mechanisms with the different initial colloidal volume fraction. The formation of the nuclei is dominant during the crystallization process at the coexistence of gas and solid. At liquid-solid coexistence the formation of nuclei and subsequent growth are observed. The crystallinity grows linearly with time, typical of interface limited growth. The observation of spontaneous growth reveals itself.
and coarsening is similar with result from the previous report by Cheng[131], where they reported the dynamics of crystallization under true microgravity conditions in the space shuttle.

In chapter seven, the hydrodynamics of droplet coalescence is discussed. We describe there the droplet coalescence in a molecular system with a variable viscosity and two colloidal systems with ultralow surface tensions. When either the viscosity is large or the surface tension is low enough, we observe that the opening of the liquid bridge initially proceeds at a constant speed set by the capillary velocity. In the first system we show that inertial effects become dominant at a Reynolds number of about $Re_c = 1.5 \pm 0.5$ and the neck then grows as the square root of time. The colloidal systems where the surface tension is lower by a factor of $10^5$ open the way to a more complete understanding of the hydrodynamics involved. The systems with ultralow surface tension are colloidal liquids. One is a colloid-polymer mixture that has phase separated into a colloid-rich liquid and a colloid-poor gas phase. The second one is the colloidal system amply discussed in this thesis: colloidal liquid droplets in equilibrium with its gas phase suspended in a homogeneous binary liquid mixture. We conclude with two weakly attractive systems: a colloid-polymer mixture and colloids in a binary mixture to complete this thesis.