Colloids are small particles (1–1000 nm) that display Brownian motion in suspension and as a result colloidal suspensions obey the same statistical physical laws as atomic and molecular fluids. Consequent colloidal suspensions show similar phase transitions, for example a fluid to crystal transition. Because of their size, colloids can be easily observed with optical microscopy. Moreover, the typical timescale on which processes occur in colloidal systems is much longer than that in atomic systems which facilitates observation of relevant physical processes. As a result, colloids are widely used as model systems to study generic processes which also occur in atomic and molecular systems but are much more difficult (if not impossible) to observe in these systems. In addition, due to their specific length scales, structures spontaneously formed by colloids have also gained interest as functional materials.

This thesis discusses the colloidal crystals formed by colloids with two different shapes, namely spheres and cubes. The investigation of colloidal crystal structures spontaneously formed by these particles in suspension, or induced by controlled solvent evaporation, forms the main focus of this thesis. Moreover, we explore several new X-ray imaging and scattering techniques that provide additional information on the colloidal crystal structures. An overview of the two systems and their (predicted) ordered structures, as well as the fabrication and characterization techniques, is presented in Chap. 1.

Part I of this thesis deals with colloidal sphere crystals in two forms: dried colloidal crystals of fixed spheres, which are of particular interest as templates for photonic structures, and colloidal crystals in suspension in which colloidal dynamics can be studied. Chapter 2 describes the preparation of dried colloidal crystals via sedimentation and convective assembly, with the aim to study the average structure and defects with synchrotron and free electron laser X-ray techniques. The special sample modifications needed for these experiments during or after preparation are presented. It is shown that for small colloidal crystal grains that need to be mounted on a fiber tip, dried crystals of silica spheres obtained via sedimentation are preferred. Furthermore, polystyrene particles are found to be deposited controllably in thin large single crystals on the specific substrates needed
for free electron laser (FEL) studies. In addition, the results are discussed of two X-ray scattering experiments performed on polystyrene crystals. The first is a pump-probe experiment of the dynamics of laser heating on the crystal structure with a FEL; the second study addresses the colloidal crystal structure melting around the glass transition temperature of polystyrene.

The colloidal crystal grains mounted on a fiber tip prepared in Chap. 2 are studied with coherent X-ray diffraction imaging (CXDI) in Chap. 3 to reveal the inner structure of the grains. In the scattering data, diffuse scattering in the form of a Bragg rod is observed, which is related to stacking defects in the sequence of the hexagonal close-packed planes. A model for the Bragg rod intensity distribution is developed that allows us to extract the stacking sequence of the crystal grain. Additionally, preliminary results from the reconstructions of the full real-space structure are presented. Both analysis methods open up ways to obtain crucial structural information from finite-sized crystalline samples by employing advanced third-generation X-ray sources.

Colloidal crystals in suspension are studied in Chap. 4 where we aim to induce defect diffusion while following the process in real space and time. A new model system is developed in which thermosensitive colloidal poly-N-isopropyl acrylamide (PNIPAM) particles are embedded into a non-thermoresponsive colloidal crystal. Laser scanning confocal microscopy (LSCM) of the crystal structures shows that a decrease in temperature can induce in situ defect movement.

Part II of this thesis deals with the colloidal crystal structures formed by micron-sized colloidal cubes with rounded edges. Their shape is described by a so-called superball that is mathematically defined as follows:

$$\frac{|x|^m}{a} + \frac{|y|^m}{a} + \frac{|z|^m}{a} \leq 1,$$

where $a$ is the particle radius and $m$ is the shape parameter that defines the roundness of the cube corners. The aim in this part of the thesis was to investigate the effect of the cube shape, the role of the $m$-value, and the various particle interactions, ranging from repulsive to attractive, on the close-packed structures that these cubes spontaneously form.

Chapter 5 describes the synthesis of three different types of colloidal cubes: hematite cubes, silica-coated hematite cubes, and hollow silica cubes. The properties of the three different cubes such as size, shape, and interaction are briefly outlined as these play an important role in Part II of the thesis.

Chapters 6 and 7 focus on the ordered structures formed by hollow silica cubes induced via convective assembly, which is a convenient method for the fabrication of ordered structures of colloids. In Chap. 6, an experimental setup is introduced that employs a thermal gradient to counteract sedimentation of the particles, which allows the fabrication of ordered structures of the cubes. Scanning electron microscopy (SEM) analysis of the structures shows that due to the strong capillary forces, cube sides are aligned with the substrate. This alignment explains that the order found in monolayers corresponds to the two optimal packings, the \( \Lambda_0 \) and the
$\Lambda_1$-lattice, as predicted by theory and simulations for 2D superball structures. Small-angle X-ray scattering (SAXS) measurements on 3D multilayer structures confirm the presence of the lattices in the layers, which appear to possess a hollow-site stacking. Chapter 7 focusses on cubes with a higher $m$-value that is a consequence of a larger cube size. Three different convective assembly methods are applied to counteract cube sedimentation. One of these methods has the advantage that the formation of ordered structures can be followed in time with optical microscopy. The analysis reveals that during structure formation, rearrangements can take place in the close-packed structures. Computer analysis of the SEM images is used to identify the local packing environment of each particle. This analysis leads to conclusive evidence that an increase in $m$ corresponds to an increase in the $\Lambda_1$-lattice packing in monolayers, as also predicted by simulations.

Motivated by the insight that repulsive particles may display phase transitions driven by entropy only, we investigate in Chap. 8 the assembly of charge-stabilized hollow silica cubes in suspension. It is shown that Debye screening length influences the self-assembly of the cubes in aqueous suspensions and a critical Debye length ($\sim 48$ nm) is identified above which crystallization can occur. The dense crystalline sediments that are obtained under gravity are investigated in detailed with SAXS. These measurements show that although the cubes are aligned to the capillary walls, the formed structures still seem to be in agreement with the equilibrium structures predicted by simulations of hard cubes.

In Chap. 9, the focus is shifted to the hematite cubes with a permanent magnetic dipole moment to study the effect of the dipole–dipole attractions on the cube assembly into sedimentary crystals. Detailed SAXS investigations reveal that by increasing the double-layer repulsion, which opposes the magnetic dipole–dipole attractions and Van der Waals attractions, ordering can be induced in the cube sediments. In different solvent and/or salt conditions, the structures can be tuned from short-range-ordered polycrystalline sediments to long-range-ordered layered structures of cubes. In addition, the assembly can be directed by the presence of an external magnetic field, which is found to induce the formation of a single body-centered monoclinic (BCM) crystal structure that possesses true long-range order. Surprisingly, a rotation of the BCM structure is found to occur in the lower parts of the sediments as a consequence of the increased osmotic pressure, which destroys the alignment of the cubes in the magnetic field.
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