Long range order in 3D nanoparticle assemblies

Elisabeth Josten
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Abstract

Magnetic nanoparticles and their assembly in highly correlated structures are of great interest for future applications as e.g. spin-based data storage. These systems are not only distinguished by the obvious miniaturization but by the novel physical properties emerging due to their limited size and ordered arrangement, as well. The superstructures are formed from nanometer sized building blocks, ordered like atoms in a crystal, which renders them a new class of materials. To gain a profound understanding of these systems it is necessary to perform experiments on all length scales.

The present work supplies an extensive and novel contribution to the investigation of the structural properties and the self-assembly of iron oxide nanoparticle superstructures. The unique combination of microscopy and scattering techniques allows a new understanding of the structural features of three dimensional structures that develop from the self-organization of these particles.

In this thesis, magnetic nanoparticles have been deposited for this purpose using a self-organization method to form long range ordered structures, so called mesocrystals. The process of self-assembling has been investigated for the influence of different deposition parameters and these parameters have been optimized. An in-situ study using grazing incidence x-ray scattering during the growth of the mesocrystals allowed the identification of different stages of the mesocrystal growth and its spatial position. From the combination of these different experiments it was possible to establish a model for the growth process governed by a shape and size selective arrangement of the particles.

Another highlight of this work is the measurement on a single mesocrystal, which had only a volume of $2.5 \, \mu m^3$, leading to a challenging diffraction experiment. It was possible to extract structural quality parameters from this investigation, as e.g. the mosaicity, which would normally be masked by the distribution of the orientation and lattice parameters generally present in the normal samples that contain a large number of mesocrystals.

A detailed analysis of the scattering patterns of different samples with mesocrystal ensembles yielded a refined structure model, which allowed the quantitative analysis of the data collected as well for in-situ created as for already deposited samples. In addition, a new rounded cubes form factor was developed for the modeling of small angle x-ray scattering and the single mesocrystal diffraction data.

In conclusion, this work shows the large correlation in these nanoparticle superstructures, the distribution of different structural parameters that can be present in the samples and how much information can be extracted from the scattering patterns.
Langreichweitige Ordnung in 3D Nanopartikelüberstrukturen

Zusammenfassung


Eine neu entwickelte detaillierte Analyse von Streubildern des Ensembles führte zu einem neuen, verfeinerten Strukturmodell, welches zur quantitativen Untersuchung der in-situ hergestellten und auch der bereits deponierten Proben herangezogen wurde. Weiterhin wurde ein neuer, abgerundeter kubischer Form Faktor vorgestellt, der für die Modellierung abgeschnittener Würfel sowohl für Röntgenkleinwinkelstreuung als auch in der Streuung an einem einzelnen Mesokristall verwendet wurde.

Zusammenfassend zeigt diese Arbeit, wie hoch korreliert die einzelnen Nanopartikelüberstrukturen sind, welche Verteilung die strukturellen Parameter auf den Proben haben können und wie viele Informationen aus den komplexen Streubildern gewonnen werden können.
# Contents

## 1 Introduction

## 2 Theoretical Background

2.1 Properties of magnetic nanoparticles

2.1.1 Brownian motion

2.1.2 Magnetic single-domain nanoparticles

2.1.3 Superparamagnetism

2.1.4 Interactions between nanoparticles

2.1.4.1 Van der Waals interaction

2.1.4.2 Gravity and external magnetic field

2.1.4.3 Dipole-dipole force

2.1.5 Free energy

2.2 Scattering methods

2.2.1 Fundamentals

2.2.2 Interaction of radiation with matter

2.2.3 Nanoparticles and assemblies

2.2.4 Influences of the measurement method and structural imperfections

2.2.5 Structures on surfaces

## 3 Experimental Methods

3.1 Light microscopy

3.2 Scanning electron microscopy

3.3 Transmission electron microscopy

3.4 Atomic force microscopy

3.5 X-ray reflectometry

3.6 Small angle X-ray scattering

3.7 Grazing incidence small angle X-ray scattering

3.8 X-ray diffraction

3.9 Space group evaluation of GISAXS data

## 4 Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

4.1 $\gamma$-Fe$_2$O$_3$ nanoparticles

4.1.1 Preparation

4.1.2 Structural characterization

4.2 Self-assembly of 3D ordered nanoparticles

4.2.1 Sample preparation

4.2.2 Model for the mesocrystal growth

4.2.3 Ensemble of mesocrystals
### 4.2.4 Influence of deposition parameters on the mesocrystal characteristics

- **4.2.4.1 Nanoparticle shape**
- **4.2.4.2 Magnetic field**
- **4.2.4.3 Evaporation time**
- **4.2.4.4 Extraordinary Conditions**

### 4.2.5 Crystalline orientation of the nanoparticles

### 5 Modeling of scattering intensities of 3D nanoparticle assemblies

- **5.1 General considerations**
  - **5.1.1 Single mesocrystal structure factor in Born Approximation**
  - **5.1.2 Influence of 2D powder and mesocrystal ensemble statistics**
- **5.2 Grazing incidence specific considerations**
  - **5.2.1 Substrate reflection**
  - **5.2.2 Refraction**
  - **5.2.3 Inhomogeneity**
- **5.3 Model implementation**
  - **5.3.1 Single mesocrystal modeling**
  - **5.3.2 Peak shape computation for in-situ experiments**
  - **5.3.3 Reflectivity modeling**
  - **5.3.4 Lógos and BornAgain (work in progress)**
- **5.4 Conclusions**

### 6 Time evolution of mesocrystal growth

- **6.1 Development of the in-situ cell**
- **6.2 Experimental details**
- **6.3 Results and discussion**
  - **6.3.1 Qualitative analysis of the data**
  - **6.3.2 Data evaluation**
  - **6.3.3 Four stages of the mesocrystal growth**
- **6.4 Conclusions**

### 7 Diffraction from a single mesocrystal

- **7.1 Separation of a single mesocrystal**
- **7.2 Experimental details**
- **7.3 Result and discussion**
  - **7.3.1 Analysis of the scattering pattern**
    - **7.3.1.1 Structure**
    - **7.3.1.2 Lattice constant and correlation length**
    - **7.3.1.3 Laue oscillation**
    - **7.3.1.4 Simulation of the scattering pattern**
  - **7.3.2 Crystal structure analysis**
    - **7.3.2.1 Rocking scans**
    - **7.3.2.2 Integrated intensities**
- **7.4 Conclusions**

### 8 Conclusion and outlook
A Additional Figures and Tables
A.1 Appendix for chapter 4 ................................. 151
A.2 Appendix of chapter 6:
  Time evolution of mesocrystal growth .............................. 161
A.3 Appendix of chapter 7:
  Diffraction from a single mesocrystal ............................ 163
  A.3.1 Scattering patterns ........................................ 163
  A.3.2 Lattice constant and correlation lengths .................... 166
  A.3.3 Simulations ................................................ 167
  A.3.4 Rocking scans and integrated intensities ................... 170

B Used algorithms
B.1 Form factor fit for integrated intensities .......................... 177
B.2 Laue function fit for single mesocrystal ............................ 187
B.3 Single mesocrystal modeling ...................................... 188
B.4 Peak shape computation for in-situ experiments ................... 190
B.5 GeniX plugin for a reflectivity simulation of an ensemble of mesocrystals 202

C Bibliography

D List of Figures

E List of Tables

F List of Symbols, Abbreviations and Definitions
  F.1 Symbols ...................................................... 231
  F.2 Abbreviations ............................................... 234
  F.3 Definitions .................................................. 236

Acknowledgement
Chapter 1

Introduction

Two thousand years ago in Greece, lodestone was discovered, a naturally occurring magnetized mineral known today as magnetite [1]. This finding marked the beginning of a new scientific era: the research on magnetism. Mankind’s curiosity to comprehend, explain and make use of this phenomenon had been piqued. Today, the optimization and further development of products based on magnetism is still a field of immense interest to science and technology. An example, taken from the last few decades of research, of the application of magnetism in daily life is the giant magnetoresistance (GMR) effect used in today’s hard disc drives. This phenomenon was observed independently by Peter Grünberg and Albert Fert in 1988, who were awarded with the Nobel Prize in Physics in 2007 for their work in this area [18, 23]. The application of this effect allows the construction of smaller magnetic field sensors with higher sensitivity. These sensors have successfully been implemented as read heads in hard disks with highly increased data density. The effect utilizes the change of resistance depending on the relative alignment of the magnetization inside two ferromagnetic layers, which are separated by a non-magnetic layer.

Fundamental research on magnetic nanostructures is an important part of the current scientific efforts in spin-based information technology [63]. The goal is to reach a higher readout rate and also an increase of the bit density in data storage, which continuously requires miniaturization. Self-assembled structures of nanocrystals are promising candidates for a new generation of magnetic storage media [43], in which a single particle represents one information unit. To build even higher density magnetic storage devices in the future using the approach of today’s standard devices of a two-dimensional media, would require that ferromagnetic single domain nanoparticles, magnetically decoupled, order perfectly on a two-dimensional lattice. The process of such self-organization is a relevant scientific question, which becomes even more interesting and more challenging to investigate when it involves three dimensions. For applications, the magnetic properties of the nanoparticles and the correlations inside their lattice play a significant role, as neighbouring bits should not influence each other.

In addition to novel optical and electronic properties found in nanoscale materials these particles exhibit exciting magnetic characteristics induced by the increased surface-to-volume ratio. Below a critical particle size, which is material-specific (e.g. a diameter of 15 nm for Fe, 35 nm for Co and 30 nm for γ-Fe₂O₃ [20]), the development of domain walls is energetically unfavorable and the nanoparticles consist of only a single magnetic domain. Another important property of these particles is superparamagnetism caused by the instability of the magnetization due to thermal excitations [20]. Furthermore, many nanoparticles possess the capacity to assemble into long-range ordered structures, organizing spontaneously in superstructures without external intervention [94]. Inside such an assembly, where the particles are separated by an organic
shell, the long-ranged dipole-dipole interaction is expected to be the only magnetic interaction as the direct electronic exchange interaction between them through the ligand shell is negligible [20].

In order to reach further miniaturization for data storage and avoid greater loss of information, the superparamagnetic limit must be overcome. This can be achieved, for example, using larger magnetic anisotropies; the dipole influences of neighbouring particles must be limited and the self-assembling process must be reliable. Success was first achieved by Sun et al., who prepared ferromagnetic nanoparticle superstructures, which can be used as small nanomagnets to store information [89]. Further possible applications of these systems are magnetic field sensors with superparamagnetic nanoparticle assemblies reaching high sensitivities with extremely small sensing volumes. Applications in other scientific fields are possible e.g. in biology and medicine, in terms of treatment for hyperthermia, drug-delivery and cancer treatment. Research in the field of nanoparticles has increased in the last few decades with advances in nanoparticle synthesis and new possibilities for its investigation. Intensive research on the magnetic properties of single particles as well as nanoparticle clusters and the process of self-assembly is necessary for all these applications.

The investigation of the phenomenon of self-assembly and the resulting nanoparticle superstructures has opened up a new field in science. Not only have nanoparticles been identified as a novel type of material with special properties, but nanoparticle superstructures are now recognized as a new class of ordered systems, where the particles order in a similar way to atoms in a solid. Nanoparticle superspins (single domain magnetic moments) correspond to atomic spins and the nanoparticle superlattices (or supercrystals, mesocrystals,..) are the analogous to crystals. S.C. Glotzer and M.J. Solomon pointed out the importance of these systems by commenting "These new particles are poised to become the ‘atoms’ and ‘molecules’ of tomorrow’s materials" [46]. The novelty of the new systems is the nm dimension of the building blocks that raises many new questions and high hopes for new scientific findings of new properties and possible applications.

To acquire insights into the basic physics in these systems, experiments on all length scales must be performed. This dissertation aims at contributing to the comprehension of self-assembly and the structural properties of γ-Fe₂O₃ nanoparticle ensembles, using the combination of a variety of advanced microscopy and scattering methods. Complex scattering experiments were performed yielding new and fascinating insights, adding more and more aspects to the understanding of the subject. With these methods the structural properties of the nanoparticle superstructure could be investigated three dimensional and depth resolved over a large area of the sample.

For the experiments in this thesis, well known γ-Fe₂O₃ particles were used, which have a sizable magnetization, can be reproduced at high quality [14, 15] and which have already been investigated in terms of their atomic structural and magnetic properties [33, 34, 103]. Furthermore it was known that these particles could be grown in ensembles of 3D superstructures, called mesocrystals [33, 35]. These known characteristics are the basic requirements for advanced experiments on nanoparticle superstructures and thus for this dissertation. Iron oxide particles are used to guarantee a stable system, as these are relatively insensitive to oxygen and moisture from the environment and permit an easy sample handling.

One goal of this PhD thesis is to understand and control the process of self assembly in more detail. Thus the influence of different preparation parameters on the mesocrystals characteristics is
investigated and the feasibility of tuning the ensemble of grown mesocrystals using external parameters such as particle shape, magnetic field and evaporation time is shown. An optimization of the sample preparation was realized. Conditions have been identified under which the process of self-assembly leads to shape-selective self-segregation during the drying of the droplet and this result is the first direct observation of well-separated 3D ordered structures within one sample. Using an extreme magnetic field configuration, a nanoparticle macro-polyccrystal in the mm-range was grown for the first time. All these experiments undertaken to achieve a profound understanding and optimization of the ensemble of mesocrystals can be found in chapter 4.

An in-situ GISAXS study during the drying process was carried out to gain a deeper understanding of the process of time-dependent self-assembly (chapter 6). To carry out this experiment, a specialized in-situ cell with several extra components was built to ensure precise control of the system and the possibility of an accurate identification of key influences. Therefore new insights into the drying and self-assembly process of an ensemble of 3D highly ordered assemblies were gained and four stages of the mesocrystals growth could be identified.

A highlight of this work is the diffraction experiment on a separated single mesocrystal (chapter 7). With the outstanding intensity and precision of state-of-the-art synchrotron beamlines it is possible to push the already established limits in diffraction from Å-size [39, 57, 78, 79] and mm-size unit cells [62, 97] further to 10 nm large building blocks with samples of only 2.5 µm³ scattering volume. So far, the smallest crystals investigated in the atomic structure are reported to have a volume in the 10³ µm³ range [16, 17, 48]. The achievable data quality is, as expected, not yet comparable to conventional single crystal XRD. Nevertheless a lot of new information could be gained complementary to GISAXS on a 2D powder of mesocrystals. A quantitative structural analysis of a single mesocrystal was performed, revealing the mosaicity in the range of good atomic crystals, extracting the lattice constant and size distribution inside one mesocrystal. This challenging experiment proved the feasibility of the investigation of single, small mesocrystals of nanoparticles and opened a new field for further investigations of mesocrystal properties.

For a more detailed analysis of the scattering patterns a new structure model was developed to interpret the time-resolved in-situ as well as the post deposition GISAXS and the single mesocrystal diffraction images (chapter 5). With the help of the new model, more features of the scattering patterns could be interpreted and a new insight in the system was gained. Furthermore the cubic form-factor was refined, which describes the integrated intensities of the single mesocrystal as well as the SAXS measurements.

Finally, all conclusions from these experiments were included in a first approach to model the process of self-assembly of an ensemble of mesocrystals with magnetic nanoparticles (chapter 4).

In this PhD thesis, it was possible with the combined effort of these various experiments to find the optimal deposition conditions to produce high-quality nanoparticle superstructures. The resulting structures have been characterized in more detail than has been done before, revealing for example a clear distinction between single mesocrystal and ensemble variations of structural parameters. A four-stage process self-organization could be identified and explained using a detailed model.
Chapter 2

Theoretical Background

This chapter gives an overview over the physics that governs nanoparticles in general and that is needed to understand the experiments performed in this work. For most of the subjects described in the following sections, a variety of literature exists which describes the theory in more detail. The literature used is referenced in the according paragraphs.

2.1 Properties of magnetic nanoparticles

The nanoparticles that have been used for our investigations are microscopic single crystals exhibiting special characteristics not present or notable in macroscopic materials. It is crucial to know the physics behind these effects especially for the understanding of self-assembly and magnetic interactions.

2.1.1 Brownian motion

When particles reside in a liquid the thermal motion of the liquids molecules leads to a random motion of the particles first observed by Robert Brown in 1827 on pollen grains and explained by Einstein in 1905 [40]. The motion of the particles follows the diffusion equation \( \frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} \). The diffusion coefficient of this motion is a function of the liquids viscosity, the absolute temperature and the particle size as given by [40]:

\[
D = \frac{R}{6\pi N_A \eta \cdot r_{NP}}
\]

(2.1)

where \( r_{NP} \) is the particle radius, \( \eta \) the friction coefficient, \( R \) the ideal gas constant, \( N_A \) the Avogadro constant and \( T \) the temperature. Obviously, larger particles will move slower and increasing temperature will speed up the motion.

The diffusion equation can be used to derive the average displacement of a particle after a given time to be [40]:

\[
\langle \Delta x \rangle = \sqrt{2Dt} = \sqrt{\frac{R}{3\pi N_A \eta \cdot r_{NP}} T \cdot t}
\]

(2.2)
This result is of crucial importance for the self organization process described in section 4.2.2 as it limits the possibility for particles to find suitable vacancies in a given time.

### 2.1.2 Magnetic single-domain nanoparticles

Below a critical size of ferromagnetic particles, the development of domain walls is energetically unfavorable and the nanoparticles consist of only a single magnetic domain. The critical radius $r_c$, which is material-specific, is given by [2, 20]:

$$r_c \approx 9 \sqrt{\frac{AK}{\mu_0 M_s^2}}$$  \hspace{1cm} (2.3)

with $\mu_0$ the vacuum permeability and $M_s$ the saturation magnetization. $K$ is the anisotropy constant, the energy density needed to rotate the magnetic moment away from a single easy axis, which is a result of the spin-orbit interaction of the electrons in the crystal lattice. $A$ is the exchange constant, which is a characteristic figure of a ferromagnetic material proportional to the microscopic exchange constant $J$ and the quantity characterizing the strength of the exchange coupling. Together, both effects determine the energy needed for the formation of domain walls and thus the maximal size of a single domain particle. Example values for the critical radius are 15 nm for Fe, 35 nm for Co and 30 nm for $\gamma$-Fe$_2$O$_3$ [20].

### 2.1.3 Superparamagnetism

Thermal fluctuations can flip the magnetic moment of magnetic materials when their size is reduced as the thermal energy gets in the order of magnitude of the magnetic anisotropy, which is responsible for keeping the magnetic moment aligned in a specific direction. This is typically the case for single domain nanoparticles, as investigated in this dissertation at room temperature. An important measure for this effect is the Néel relaxation time $\tau_N$ (eqn. 2.4) [2, 8, 12, 20, 66], which describes the average time between two flips and depends on the particle volume $V$, the anisotropy constant $K$, the characteristic attempt time $\tau_0$ of the material and the temperature $T$. When measuring the magnetic moment of a sample of such particles, this effect leads to paramagnetic like behavior described by the Langevin function $L(x)$ (eqn. 2.5) [2, 8, 20] above the so called blocking temperature $T_B$ (eqn. 2.6) [2, 8, 20]. In this case the magnetic moment is constantly flipped by thermal fluctuations so that no macroscopic magnetization can be measured without applying an external magnetic field. In this connection $N_{NP}$ is the number of particles, $m$ the magnetic moment of each particle and $H$ the external applied field. This magnetic state is called superparamagnetism.

$$\tau_N = \tau_0 \exp \left( \frac{KV}{k_B T} \right)$$  \hspace{1cm} (2.4)

$$M(H) \approx N_{NP} \cdot m \cdot L \left( \frac{\mu_0 H m}{k_B T} \right) \text{ with } L(x) = \coth(x) - \frac{1}{x}, \text{ for } k_B T \gg KV$$  \hspace{1cm} (2.5)

$$T_B = \frac{KV}{k_B \ln \left( \frac{\tau_{m}}{\tau_0} \right)}$$  \hspace{1cm} (2.6)
Below the blocking temperature a ferromagnetic hysteresis of the macroscopic magnetic moment can be measured, which can be calculated by the Stoner Wohlfarth model [2, 8, 20, 87]. As the magnetic moments flip with the Néel relaxation time, the blocking temperature measured depends on the time scale of the experiment $\tau_m$. If the timescale for the relaxation time $\tau_N$ is bigger than the experimental measuring time the system appears to be static (or so called blocked).

### 2.1.4 Interactions between nanoparticles

The process of self-assembly is governed by the interaction of different attractive and repulsive forces. The main influences on our system will be introduced in this section.

#### 2.1.4.1 Van der Waals interaction

As is possible for any molecule and bound or unbound atom, quantum fluctuation induced arbitrary electric dipole moments of nanoparticle surface atoms can induce electron displacement of another particles atoms leading to a dipole-dipole attraction of both particles, which drops with $r^{-6}$ on the atomic level, where $r$ is the distance between the atoms/molecules. An approximation for the “macroscopic” van der Waals interaction between objects consisting of many atoms/molecules is a pairwise summation of all molecular interactions inside the macroscopic bodies in dependence on their shape [24]. For example, the van der Waals potential for spherical particles with radii $r_{NP_1}$ and $r_{NP_2}$ in a center to center distance $r = r_{NP_1} + r_{NP_2} + a$, where $a$ is the distance between the surfaces, results in [24]:

$$U_{vdW}(r) = -\frac{A}{3} \left( \frac{r_{NP_1} \cdot r_{NP_2}}{r^2 - (r_{NP_1} + r_{NP_2})^2} + \frac{r_{NP_1} \cdot r_{NP_2}}{r^2 - (r_{NP_1} - r_{NP_2})^2} + \frac{1}{2} \ln \left( \frac{r^2 - (r_{NP_1} + r_{NP_2})^2}{r^2 - (r_{NP_1} - r_{NP_2})^2} \right) \right)$$

(2.7)

$A$ is the material-dependent Hamaker-constant, which specifies the effective strength of the van der Waals force. In the approximation for very close objects, where the radii of spherical nanoparticles are large compared to the distance between the surfaces ($a \ll r_{NP_1}, r_{NP_2}$), the eqn. 2.7 gets simplified to [10]:

$$U_{vdW}(a) = -\frac{A}{6 \cdot a} \left( \frac{r_{NP_1} \cdot r_{NP_2}}{r_{NP_1} + r_{NP_2}} \right)$$

(2.8)

The force of the van der Waals interaction is the negative derivative with respect to $a$. An estimate for $\gamma$-Fe$_2$O$_3$ nanoparticles with a radius of 5 nm, a surface distance of 1 nm and a Hamaker-constant of $18 \cdot 10^{-21}$ J [42] yields a force in the order of magnitude of $10^{-12} N$.

For electrically neutral particles this van der Waals interaction (vdW) is an important, often dominating, contribution to the interaction potential when in solution. All particles will have a basic interaction potential governed by their vdW attraction, which depends mainly on the surface chemical composition and size, and the electrostatic repulsion of the surface atoms at Å distances, which can be modified by other interactions in specific cases. This interplay of attractive and repulsive forces leads to a potential that always has its minimum at an particle distance comparable to the size of an atom, while the binding strength increases with the particle radius [24]. In consequence, the interaction length scale relative to the particle size decreases with
increasing radius, which has implications on the NP self organization process when changing the particle size.

2.1.4.2 Gravity and external magnetic field

In the case of iron oxide particles dissolved in toluene the buoyant force does only compensate a small fraction of the particle weight (toluene density is 0.87 \( \text{g cm}^{-3} \) compared to 5.242 \( \text{g cm}^{-3} \) of \( \gamma\text{-Fe}_2\text{O}_3 \)) leading to an effective gravitational acceleration constant \( g_{\text{eff}} \) of eqn. 2.9 for the particles in dependence to the gravitational acceleration constant \( g \), and leading to an effective force in the order of \( 5 \cdot 10^{-20} \text{ N} \) on a \((10 \text{ nm})^3 \) particle pointing towards the substrate. Together with the Brownian motion this leads to a particle concentration \( \rho \) inside the solvent which follows the barometric distribution eqn. 2.10 [5], where \( m \) is the mass of the particle and \( h \) height difference.

\[
\begin{align*}
g_{\text{eff}} &= \left( 1 - \frac{0.87}{5.242} \right) \cdot g \quad (2.9) \\
\rho &= \rho_0 e^{-\frac{mg_{\text{eff}}h}{k_B T}} \quad (2.10)
\end{align*}
\]

The second external force acting on the particles is an applied magnetic field. This will have two effects on the super-paramagnetic moment of the particles. The field itself applies a torque \( \vec{\tau} \) that tries to align the moment into the field direction (eqn. 2.11) [2, 4], which will compete with the thermal fluctuations, yielding a Langevin type behavior for the average magnetic moment as given in eqn. 2.12. In addition, any magnetic field gradient will accelerate moments aligned within the field direction with a force \( F \) given in eqn. 2.13 [2, 4]. In consequence, the superparamagnetic particles will be partially aligned by the magnetic field and dragged in the direction of the field gradient. Considering a induced moment of 1000 \( \mu_B \) in a field with gradient \( 10 \text{ mT cm}^{-1} \) leads to a force of \( 10^{-20} \text{ N} \), comparable with the influence of gravitation.

\[
\begin{align*}
\vec{\tau} &= \vec{m} \times \vec{B} \quad (2.11) \\
M(H) &\approx N_{NP} \cdot m \cdot L \left( \frac{\mu_0 H m}{k_B T} \right) \quad (2.12) \\
F &= \vec{m} \cdot \vec{\nabla} \vec{B} \quad (2.13)
\end{align*}
\]

2.1.4.3 Dipole-dipole force

The magnetic field produced by the dipole moments of individual particles introduces an additional inter-particle interaction which may be altered by an external field. The force between two dipoles is given in equation 2.15 [96], which has a component perpendicular to the connection vector \( \hat{e}_r \) (first two terms) as well as an attractive/repulsive component. The latter is strongest when both moments are aligned in parallel directions and attractive when they point
into the direction of their connecting vector $\vec{r}$.

$$ B(\vec{r}) = -\frac{\mu_0}{4\pi} \nabla \frac{\vec{m} \cdot \hat{e}_r}{r^2} \quad (2.14) $$

$$ \vec{F}(\vec{r}, \vec{m}_1, \vec{m}_2) = \frac{3\mu_0}{4\pi r^4} [ (\hat{e}_r \times \vec{m}_1) \times \vec{m}_2 + (\hat{e}_r \times \vec{m}_2) \times \vec{m}_1 - 2\hat{e}_r (\vec{m}_1 \cdot \vec{m}_2) + 5\hat{e}_r ((\hat{e}_r \times \vec{m}_1) \cdot (\hat{e}_r \times \vec{m}_2))] \quad (2.15) $$

In the absence of an external magnetic field and above $T_B$ the moments of individual particles in solution will be oriented arbitrarily. This case is very similar to the van der Waals interaction, as the field of one dipole aligns the other (induced dipole in parallel direction) leading to an attractive force. As an induced dipole is involved in this interaction it drops fast with increasing distance ($\approx r^{-6}$ as the inducing dipole field, eqn. 2.14 [2, 96], drops with the square of the distance) and effectively leads to a small correction of the van der Waals potential. An estimate of the dipole force for two interacting spherical $\gamma$-Fe$_2$O$_3$ nanoparticles without an external field results with the use of eqn. 2.12, 2.14 and 2.15 in a force of $10^{-13}$ N. This estimate was done for room temperature, particle radii of 5 nm, a center to center distance of 13 nm and a saturation moment of 10286$\mu_B$ calculated from a magnetization per iron atom of 0.72$\mu_B$ [103], a cell volume of 586 Å [72] and 8 formula units per unit cell [72]. The comparison to the van der Waals interaction shows that the dipole-dipole force is about one order of magnitude lower and therefore has less influence on the self-assembly for the considered case. In an applied magnetic field, however, the moments are aligned to the field direction as given in eqn. 2.12, leading to a much stronger attractive force between particles separated in field direction and repulsion perpendicular to it, which only drops with $r^{-4}$. This effect can lead to the formation of particle chains inside the solution as was reported in [58, 90].

### 2.1.5 Free energy

In order to spontaneously form clusters the attractive force between particles needs to overcome the free energy associated with the entropy loss due to limitation of degrees of translational and rotational degrees of freedom [24]. In other words, the thermally activated movements of the particles should not break dipole-dipole bonds between particles faster than the typical time between collision and new bond formation. This mainly depends on the range and strength of the attractive forces between individual particles and the particle density inside the solution. From a microscopic point of view this corresponds to the probability of two particles to stick together long enough to bond with additional particles and not to be broken apart by thermal fluctuations. This situation can be described by the equilibrium theory of physical clusters [9, 24], which describes the average number of $n$-sized clusters $N_n$ related to each other by the canonical partition functions. For the dimer case $n = 2$ this number relates to the number of free particles $N_1$ of spherical shape with radius $R$, interaction range $\lambda$, the interacting volume $V_\varepsilon$ and interaction strength $\varepsilon$ in a volume $V$ by [24]:

$$ N_2 = N_1^2 \left( \frac{V_\varepsilon}{8\pi V} \right) \exp \left( \frac{\varepsilon}{k_B T} \right) \quad (2.16) $$

$$ V_\varepsilon = \frac{4}{3} \pi \left[ (2R + \lambda)^3 - (2R)^3 \right] \quad (2.17) $$
To increase the number of dimers and consequently of larger clusters one therefore needs to increase the interaction strength, the interaction range or lower the available volume of the particle. For small length scale interactions ($\lambda \ll R$) this leads to a free energy difference when forming a dimer that depends linearly on the interaction strength and logarithmically on the range [24]:

$$\Delta F = -k_B T \ln(N_2/N_1^2)$$

### 2.2 Scattering methods

In this section the fundamental theory of the scattering methods used is introduced. The concept is mainly taken from [3], where the theory is described in more detail.

#### 2.2.1 Fundamentals

Scattering experiments investigate the angular dependent intensity of a defined radiation, which gets scattered by interaction with a sample. The scattered intensities detected in different directions on a detector are described by the angles $2\theta$ and $\varphi$. The geometry of a scattering experiment is shown in figure 2.1. The angular dependent detected intensity is directly proportional to the differential scattering cross section $d\sigma/d\Omega$. Equation 2.19 describes the intensity $I$ as measured over a solid angle element $d\Omega$ for a given incident beam intensity $I_0$.

$$I = I_0 \frac{d\sigma(\omega, \varphi)}{d\Omega} = I_0 |f_k(\omega, \varphi)|^2$$

Dependant on the radiation type used for the experiment the derivation of the scattered intensity and thus an expression for $d\sigma/d\Omega$ starts from the stationary Schrödinger (particles with mass) or Maxwell’s equations (photons, in the limit where a macroscopic description is appropriate), leading to the wave equation (eqn. 2.20 just with different prefactors - the gray colored term is only used for neutrons) with wave function $\Psi(\vec{r})$ and scattering potential $V(\vec{r})$ for elastic scattering processes. Elastic implies scattering without energy transfer between radiation and sample.

$$V(\vec{r})\Psi(\vec{r}) = \frac{\hbar^2}{2m_{\text{red}}} \left( \nabla^2 + k^2 \right) \Psi(\vec{r})$$

$$\Psi(r) \sim e^{ik_i \vec{r}} + f_k(\omega, \varphi) e^{i k_f \vec{r}}$$

The solution of the equation must be of the form of eqn. 2.21, describing a plane incident wave (with wave vector $\vec{k}_i$) and a second scattered wave contribution (with wave vector $\vec{k}_f$ and $k_i = k_f = \frac{2\pi}{\lambda}$ as the process is elastic). The Fraunhofer approximation can be assumed as the size of the sample is much smaller than the distance between sample and source/detector and allows the description of the monochromatic radiation as a plane wave, which is described by the corresponding wave vectors. This equation for the solution can be used to retrieve an approximate solution of the wave equation, brought into integral form eqn. 2.22, by using the
2.2 Scattering methods

Figure 2.1: General scattering geometry for a scattering event of a particle with incoming wavevector $k_i$, outgoing wavevector $k_f$ and with an outgoing angle $2\theta$. The angles $\phi, \omega$ define the angle of the sample (see figure 2.4).

plane wave ($\Psi_0(\vec{r}) = e^{i\vec{k}_i \vec{r}}$) as first approximation for the wave function and than using the result of the integral as better guess for $\Psi$.

\[
\Psi_{(n+1)}(\vec{r}) = e^{i\vec{k}_i \vec{r}} + \frac{2m_{\text{red}}}{4\pi\hbar^2} \int e^{i|\vec{r}-\vec{r}'|} V(\vec{r}') \Psi_{(n)}(\vec{r}') d^3 r'
\] (2.22)

Equation 2.22 represents a superposition of the incident plane wave - the first term - with the scattered wave - the second term. This iterative approximation is known as Born series, where the first integration is already a reasonable approximation for the case of a weak interaction potential. It assumes that the incident wave is only scattered once from the sample (potential $V(\vec{r}')$). For stronger interaction potentials and larger samples multiple scattering events and thus higher order terms of the Born series need to be taken into consideration. Using the definition of the scattering vector $\vec{Q} = \vec{k}_f - \vec{k}_i$, $e^{i|\vec{r}-\vec{r}'|} = e^{i\vec{Q} \cdot \vec{r}'}$ and the far field approximation $r \approx |\vec{r} - \vec{r}'|$ one finds that the wave function amplitude of this so called first Born approximation is the Fourier transform of the scattering potential $V$:

\[
f_k^{(\text{Born})}(\vec{Q}) = \frac{2m_{\text{red}}}{4\pi\hbar^2} \int V(\vec{r}') e^{-i\vec{Q} \cdot \vec{r}'} d^3 r' \propto \vec{F}(V)
\] (2.23)

As described in the beginning of this section, the scattering experiment measures the scattering intensity eqn. 2.19, where taking the modulus square of $f_k$ removes the phase information of this result, so it is not possible to directly conclude the scattering potential from the intensity. Therefore it is necessary to calculate the scattering intensity from a model for the scattering, which largely depends on the radiation used, the sample composition and the length scales accessible within the $\vec{Q}$-range measured in the experiment. Details of such model descriptions important for this thesis are described in the subsequent sections.

2.2.2 Interaction of radiation with matter

The following paragraphs will address the basic interactions between the X-rays and the matter in the sample, which is the basis for the models used to analyze the scattered intensity. As the
scattering amplitude is connected to the potential by a Fourier transform integral, it is possible to build up the scattering amplitude starting from the atoms, when the scattering cross section for each atom is known. Therefore the discussion will focus on the derivation of the single atom scattering cross section, the atomic form factor.

The Coulomb force accelerates electrons inside the electromagnetic field of the X-ray wave, making them a source of radiation themselves. This results in the single electron Thomson scattering cross-section equation 2.24 with the classical electron radius $r_e = \frac{e^2}{4\pi\varepsilon_0m_ec^2}$ and polarization vectors of the incoming and outgoing wave $\hat{e}_i/f$, always perpendicular to the wave vectors $\vec{k}_i/f$.

$$\frac{d\sigma}{d\Omega_{\text{Thomson}}} = r_e^2 (\hat{e}_i \cdot \hat{e}_f)^2$$ (2.24)

As photons are preponderantly interacting with the electrons of the sample, the atomic form factor of the scattered X-ray wave is proportional to the Fourier transform of the charge density distribution $\rho_e$ within the atom (eqn. 2.25). This is valid for electrons bound in an atom and high photon energies compared to the binding energy.

$$f_0(\vec{Q}) = \frac{r_e}{e} \int_V \rho_e(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$ (2.25)

When measuring at low angles and therefore small $\vec{Q}$ values this cross section is proportional to the atomic number $Z$. Consequently, the elemental composition and density is the determining factor for the contrast (variation of scattering potential) in small angle X-ray experiments [110]. In the case of higher angle diffraction, on the other hand, the electron distribution of the atom needs to be taken into account, but generally is substituted by an empirical approximation to the real distribution function as can be found in e.g. [6]:

$$f_0(\vec{Q}) \approx \frac{4}{\varepsilon_0^2} \sum_{j=1}^{4} a_j e^{-b_j(2\pi\vec{Q})^2} + c$$ (2.26)

Obviously, the scattering cross section drops for large values of $\vec{Q}$. In addition, the polarization dependence of the Thomson scattering needs to be taken into account, leading to an additional polarization dependent prefactor for the scattered intensity:

$$(\hat{e}_i \cdot \hat{e}_f)^2 = \begin{cases} 
1, & \text{polarization } \perp \text{ scattering plane} \\
\cos^2(2\Theta), & \text{polarization } \parallel \text{ scattering plane} \\
\frac{\cos^2(2\Theta)}{2}, & \text{unpolarized}
\end{cases}$$ (2.27)

The deviation of the atomic form factor from the equations above due to absorption effects is known as anomalous scattering factor or anomalous dispersion correction [51]. The atomic form factor $f$ is given by [51]:

$$f(\vec{Q}, E) = f_0(\vec{Q}) + f'(E) + i f''(E)$$ (2.28)

where $f_0$ is the known Thomson scattering factor, $f'$ the real part and $f''$ the imaginary part of the anomalous scattering factors. The large absorption $\mu$ of X-rays (compared to neutron...
scattering) has to be taken into account. It enters the atomic form factor as an imaginary part proportional to the absorption length\(^1\) \(\mu\) and to the absorption cross-section \(\sigma_{\text{abs}}\) via

\[
\mu = \rho_{\text{atom}} \sigma_{\text{abs}} = \rho_{\text{atom}} 2 r_0 \lambda f''(E).
\] (2.29)

### 2.2.3 Nanoparticles and assemblies

In contrast to the case of atomic crystals, the size of nanoparticle building blocks in the investigated structures is relatively large compared to the typical wavelength used in X-ray experiments, which are in the order of Å. Therefore the investigations on nanoparticle superstructures are carried out at small \(\vec{Q}\) values and therefore small angles. The atomic crystal structure inside the nanoparticle can be probed with wide angle scattering as is the case for solids with structures on the atomic length scale.

Here we focus on such experiments carried out at small angles, as most of the measurements done in the scope of this dissertation were carried out in such a geometry\(^2\). In this case one only observes the area of reciprocal space\(^3\) which is insensitive to the atomic structure of the system and can work with a smooth scattering potential derived from the atomic density instead of using the full atomic structure. For most nano-sized objects this density will be constant over large regions of the particle. In our case of iron oxide nanoparticles this would be the constant scattering power density of \(\gamma\)-Fe\(_2\)O\(_3\) inside the particle with a small organic shell of smaller scattering power. The Fourier transform integral is additive, so one can retrieve the scattering cross section by adding up the Fourier transforms of each component separately. The part of the scattering cross section that is defined from a single particle scattering potential is called single particle form factor. It can be measured directly on particles in a dilute solution as there is no interference between scattered waves from different particles with distance far greater than the coherence length of the radiation. The form factor functions for shapes relevant in this thesis are given in chapter 5.

For densely packed particles inside an assembly, interference between individual particles is not negligible any more and the combined scattering potential of the particles needs to be taken into account. To simplify the model one can make use of the convolution theorem for Fourier transforms (eqn. 2.30) to separate the single particle from the lattice contribution.

\[
\mathcal{F}(A \ast B) = \mathcal{F}(A) \cdot \mathcal{F}(B)
\] (2.30)

In general the nanoparticle superstructure in real space can mathematically be described as a convolution of the nanoparticle scattering potential in a basis defining the nanoparticle positions and an infinite lattice (see figure 2.2). For the scattering the convolution theorem can be used, as each corresponding element can be separately Fourier transformed and the results in reciprocal space only need to be multiplied afterwards [3]. If the assembly consists of similar particles (or unit cells of atoms in crystals) arranged in a regular lattice pattern, the form factor included in the unit cell structure factor and lattice contribution can be separated by individually transforming each contribution to get eqn. 2.31, as the real space structure is a convolution of a particle with the lattice position.

\(^1\)Typical absorption lengths are in the order of \(\mu\)m for hard X-rays.
\(^2\)The description of atomic crystals for larger scattering angles is carried out analogously.
\(^3\)the Fourier transform of real space
Figure 2.2: Application of the convolution theorem to simplify the modeling and allow a model independent understanding of a scattering experiment.

\[
S(\mathbf{Q}) \sim \sum_j f_j(\mathbf{Q}) e^{i\mathbf{Qr}_j} \cdot \sum_{h,k,l} \delta(\mathbf{Q} - (ha_1^* + ka_2^* + la_3^*))
\]  
(2.31)

This means that the scattering pattern of an infinite lattice of particles consists of delta functions with intensities modulated by the single particle form factor. If the lattice is finite (which means it is a product of an infinite lattice with some kind of box function), the lattice term has a Fourier transform, which again can be derived using the opposite direction of the convolution theorem, leading to peak shape functions at the same position as the infinite lattice delta functions (see figure 2.2 external boundaries). These peak shapes correspond to the Fourier transformation of the outer shape of the assembly. The monodispersity of the particles allows one to describe the cross section as a product of form factor and structure factor [71] (local monodisperse approximation [70]), thus the form factor part can be separated from all lattice contributions in eqn. 2.31 and it is possible to derive the pure lattice contribution directly from a measurement by dividing by a known particle form factor.

### 2.2.4 Influences of the measurement method and structural imperfections

For real experiments, there are several aspects which need to be taken into account to derive the true peak intensity and shape. Even for a perfect crystal the peak shape is not described by a delta function and a minimal peak width is present due to the instrumental resolution. This resolution is dependent on the angular uncertainties due to the collimation apertures and the finite size detector elements, as well as the wavelength spread determined by the monochromator. The limited coherence of the radiation is larger than a single mesocrystal and only becomes relevant when looking at crystal ensembles (see chapter 5).

For a diffraction experiment an intensity correction of individual reflection’s integrated intensities is necessary due to the measurement geometry. The corresponding scaling term is called...
Figure 2.3: Schematic view of an Ewald sphere.

Lorentz-factor [85]:

\[ L = \frac{1}{\sin(\theta) \cdot \sin(2\theta)} \]  

valid in this form only for measurements, where the sample is rotated in the scattering plane by the angle \( \omega \) (see figure 2.4). The effect can be described very well in the framework of the Ewald construction shown in figure 2.3.

The Ewald sphere illustrates all possible elastic scattering processes, as it constructs any orientation of the vector \( \mathbf{k}_f \) with the same length \( |\mathbf{k}| \) as the vector \( \mathbf{k}_i \). In this construction the Bragg condition \( 2d_{hkl} \cdot \sin(\theta) = n\lambda \) (or \( Q = G(hkl) \)) is fulfilled for each reciprocal lattice point on the sphere’s edge when the reciprocal space origin is placed at the end of \( \mathbf{k}_i \). Obviously, a single crystal has to be rotated around the \( \omega \)-axis to observe different Bragg reflections.

The Ewald sphere has a finite thickness \( \Delta k \) due to the finite instrument resolution. When rotating the sample (and therefore the reciprocal lattice) the movement of reciprocal lattice points through the circle arc gets faster for larger \( |\mathbf{Q}| \sim \sin(\theta) \) as illustrated in figure 2.3. In addition, the time of the reflex on the arc depends on the \( \omega \) position, where the reciprocal lattice point overlaps the Ewald sphere. For \( 2\theta = 90^\circ \) the reflection moves through the sphere almost radially, while for \( 2\theta = 180^\circ \) the movement is tangential and therefore the intersection area is larger than for the former case. These two effects combined lead to the Lorentz-Factor (eqn. 2.33) given in the last paragraph.

In addition to the considerations given above, sample influences can impact the reflection intensities and shapes. Different imperfections can influence the scattering result and are categorized into local and global imperfections. A local imperfection is an arbitrary offset of an individual
particle from its perfect lattice position and can be described by the Debye-Waller factor,

\[ I(Q) \propto |S(Q)|^2 \cdot e^{-\frac{1}{3}|Q|^2\langle u^2 \rangle}, \quad (2.34) \]

derived for the equivalent case of thermal atomic displacements for atomic crystals and is multiplied additionally to the scattering intensity \( |S(Q)|^2 \) lowering the intensity for higher Q’s. Global imperfections can be grain boundaries, stacking faults or e.g. large scale lattice deformations. They are limiting the coherence of the nanoparticle superstructure. The limitation of the structural coherence is described through the correlation length \( \varepsilon \)

\[ P(r) = e^{-\frac{r}{\varepsilon}}, \quad (2.35) \]

which statistically describes how fast the two particle correlation function vanishes with the spatial particle separation \( r \). The correlation is reduced by \( \frac{1}{\varepsilon} \) at a distance of the correlation length \( \varepsilon \). Further details on the influence of different imperfections on the scattering pattern for the system used can be found in chapter 5.

### 2.2.5 Structures on surfaces

Nanoparticle structures, as the ones described in the last section, are generally produced on top of large substrate surfaces and consist of relatively low amounts of material. To be able to characterize these structures different kinds of grazing incidences scattering techniques are applied: The specular reflectivity, off-specular scattering (figure 2.5) and grazing incidences small angle scattering (GISAS) (figure 2.6). Common to all these three techniques is that the incident beam hits the sample under a small angle \( \alpha_i \) and is scattered from the surface under the angle \( \alpha_f \) with a possible in-plane scattering angle \( \varphi \). The components of the scattering vector...
The specular reflections are observed at $\alpha_i = \alpha_f$ and $\phi = 0$, giving information parallel to the substrate’s surface normal in the nm-range such as layer thicknesses, roughnesses, or layer sequence. Off-specular scattering ($\alpha_i \neq \alpha_f$ and $\phi = 0$) gives additional information in-plane in beam direction in the μm-range. For an optimal characterization of the nanoparticle superstructure in both directions, GISAS (in general $\alpha_i \neq \alpha_f$ and $\phi \neq 0$ is possible) experiments were performed, achieving an additional nm resolution in-plane perpendicular to the beam with an angular resolution in two dimensions. In the GISAS case the specular reflectivity is detected at point (1) in figure 2.6, the off-specular scattering on a line perpendicular to the sample horizon on the detector plane at e.g. (2) and arbitrary reflections are observed at e.g. (3) with $\phi \neq 0$. The Yoneda\textsuperscript{4} line is detected at $\alpha_f = \alpha_c$, with $\alpha_c$ the critical angle of total reflection.

For all approaches, the incident beam gets close to the sample angle of total external reflection, where the prerequisite of a small scattering probability used to derive the Born approximation no longer holds. Therefore the intensity can no longer be described by the Born approximation. To be able to analyze the scattering intensity one can use a two step approach by separating the sample into layers of average scattering potential, where the wave equation 2.20 is solved exactly with an optical approach, and than introducing in-plane deviations from this average as small perturbation, treatable with the Born approximation. This so called Distorted Wave Born Approximation (DWBA) leads to several Fourier transform components for the in-plane structure for each possible wave propagation inside the medium.

The treatment of the average potential uses the result of a wave traveling across a potential step $V(z)$, getting partly reflected and transmitted according to the Fresnel coefficients, well known from optics or quantum mechanics:

$$r_{j,j+1} = \frac{k_{z,j} - k_{z,j+1}}{k_{z,j} + k_{z,j+1}}$$

with $k_{z,j} = k_0 \sqrt{n_j^2 - \cos \alpha_j^2}$ (2.39)

$$t_{j,j+1} = \frac{2 \sqrt{k_{z,j} k_{z,j+1}}}{k_{z,j} + k_{z,j+1}}$$

and $n_j = 1 - \delta + i\beta$ (2.40)

Here the scattering power density $\delta$ and absorption $\beta$, derived from the atomic density and the low $\vec{Q}$ form factors, leads to the reflective index $n$. These single interface parameters can be used in an iterative approach introduced by Paratt [69] to derive the reflection and transmission coefficients $R_j$ and $T_j$ used in the DWBA:

$$X_j = \frac{R_j}{T_j} = e^{-2ik_{z,j} \zeta_j} \frac{r_{j,j+1} + X_{j+1}e^{2ik_{z,j+1} \zeta_j}}{1 + r_{j,j+1}X_{j+1}e^{2ik_{z,j+1} \zeta_j}}$$ (2.41)

\textsuperscript{4}a surface wave, containing mainly information about the lateral structure
Figure 2.5: Geometry of a specular and off-specular scattering experiment.

Figure 2.6: Geometry of a grazing incidence small angle scattering experiment (GISAS).
To solve the equation one can start from the substrate, which imposes the boundary condition $X_N = R_N = 0$, working upwards layer by layer up to the surface where the second boundary condition $T_0 = 1$ yields the absolute value of all coefficients. The surface reflectivity index $R_0$ yields the intensity of a reflectivity experiment, where the scattered beam has the same angle to the substrate as the incident beam (specular condition). Therefore the reflectivity experiment only measures the average scattering power density of these layers. Rough interfaces between layers can be introduced by a Debye-Waller type modification of the Fresnel coefficients as described in [30]:

$$r_{j,j+1}(\sigma) = r_{j,j+1}(0)e^{-2\sigma^2}\kappa_{j,j+1}$$

(2.42)
Chapter 3
Experimental Methods

The structural and magnetic investigation of three dimensional assemblies of nanoparticles necessitates the application of several complementary advanced methods. Scattering methods are powerful tools to look at the average correlations on a large sample area with depth resolution. Microscopy, on the other hand, yields a snapshot of the surface structure in a specific, small area. For the comprehension of the structure of such complex systems, only the combination of microscopy (e.g. SEM, TEM, AFM, ...) and x-ray scattering methods (e.g. diffraction, GISAXS,...) leads to a complete picture. A precise determination of the complete 3D structure is necessary in order to understand the magnetic correlations present in the nanoparticle superstructures.

In this chapter, the methods and instruments used to investigate the complex assemblies are described. Microscopy techniques characterize the morphology in real space imaging. For example, Scanning Electron Microscopy (SEM) visualizes information about the nanoparticle superstructure, topography, material and larger structures on the surface of the sample, while Transmission Electron Microscopy (TEM) illustrates these properties inside a crystal and additionally gives information about the atomic structure and the shape of single particles. Atomic Force Microscopy (AFM) was used to obtain the height profile of the samples as well as an independent check of the lateral size of the mesocrystals grown, an estimate of their shape and the mesocrystal density on the substrate in comparison to the SEM. For a first, not too time-consuming, check of the mesocrystal distribution on the substrate optical Light Microscopy (LM) was utilized. These methods give a local view on the mesocrystals and their supercrystal structure in real space and yield important sample parameters such as the height of the mesocrystals.

A depth resolved structural characterization over a large sample area can be achieved with X-ray scattering experiments. For this work, a study of the morphology of the individual nanoparticles in a solution was done with Small Angle X-ray Scattering (SAXS). Nanoparticle superlattices were investigated by Grazing Incidence Small Angle X-ray Scattering (GISAXS) in either lateral or specular directions, giving information on the structure of the mesocrystals. X-ray reflectometry was used to investigate the correlations along the direction of the substrate’s surface normal in the nm range with high intensities. In contrast to the small angle techniques, the x-ray diffraction method allows the study of correlations on the atomic scale and thus was used to analyze the crystal structure within the nanoparticles and their orientations in the assembly.


3.1 Light microscopy

Optical Microscopy using a LEICA INM100 system was performed to investigate the mesocrystal distribution on the substrate, as scanning electron microscopy techniques often have a too high magnification to get a good overview and are too time-consuming for large samples. A light microscope works with visible light and an optical lens system to magnify small structures. We worked in a magnification range from 50x to 1000x with a theoretical resolution from 1.8 µm to 0.3 µm, using bright field contrast imaging. The real resolution is lower due to the usage of white light and imperfections of the optical setup and can be estimated to be 1.5 to 2 times worse. The mesocrystals of a few µm size were big enough to be observed with the light microscope (see figure 3.1). The optical microscope is a fast and efficient way to test if mesocrystals have grown and to have a look at their distribution on the sample surface.

![Figure 3.1: Example picture of a light microscope image with 50x magnification and a resolution of 1.8 µm (inset: 1000x, 0.3 µm).](image)

3.2 Scanning electron microscopy

The Scanning Electron Microscope (SEM) works in reflection mode, scanning a focused electron beam over the sample and measuring the flux of scattered electrons to create an image. The image contains information about the topography as well as about the material composition as the interaction of the electrons is element dependent. For imaging, the low energy Secondary Electrons (SE) emitted from the sample after an inelastic scattering process and the high energy BackScattered Electrons (BSE), which are fully elastic scattered, are utilized. The SE escape due to the impact of the primary electrons from the upper atomic layers and thus the surface atoms determine the image contrast, so that edges appear bright and cavity dark [105]. The information about the bulk material is deduced from the BSE intensity, which depends on the atomic number of the material [105]. The intensity of the interaction signal is measured with spatial resolution and is illustrated with variations in luminosity on the SEM picture. More information about this technique can be found in [13, 105].

In this work the SEM was used to probe a bulk sample of self-assembled mesocrystals on a substrate from the top. It yielded the lateral size of the mesocrystals grown, the mesocrystal density on the substrate surface, an estimate of their shape as well as in higher magnification (≥250000) the 2D order of the single particles at the top of a mesocrystal. This method allowed us to receive a first surface sensitive characterization of the quality of the crystal structure without destroying or cutting the sample. These intact samples could be used for further investigation where we needed the full size samples e.g. for neutron scattering. The SEM investigation was done in collaboration with Elke Brauweiler-Reuters and Hans-Peter Bochem from the Helmholtz Nanoelectronic Facility (HNF).
3.2 Scanning electron microscopy

(a) SEM image made with TLD detector with electrons from the near surface area. Burning points and a blurry view are visible.

(b) SEM image made with vCD detector with electrons from deeper parts under the organic shell. The picture has a better contrast and the structure is clearly visible.

Figure 3.2: Comparison between SEM pictures using the TLD and the vCD detector. The pictures have been recorded simultaneously.

Figure 3.3: The sample structure before the plasma treatment, where the structure can only be estimated. The picture inset shows an equivalent position of the same sample after applying the plasma. A good contrast between the nanoparticles is visible.
The earlier SEM images presented in this dissertation were obtained using a Gemini 1550VP SEM from Zeiss. This instrument has a typical resolution of 1 nm at 20 kV [106] and uses a high resolution in-lens detector (TLD). For the imaging it was operated at 20 kV in the high resolution mode at a working distance between 2 and 3 mm. For the sample characterization we recorded routinely pictures with different magnifications at several positions on the sample surface to get a good overview over the mesocrystal structures and order on every sample.

At a later stage of this work a new SEM was available. The Magellan 400 SEM from FEI offers a nanometer resolution over the full 1 keV to 30 keV electron energy range [104]. It allowed us to use a lower acceleration voltage for higher resolution, surface sensitive information [104] and a lower probability for sample damage. An Everhart Thornley detector (ETD) for secondary electrons was used for lower magnification. Images with higher magnification were recorded with an in-lens detector (TLD) for secondary electrons. The operation mode used was 10 kV with a working distance of around 4 mm. The characterization procedure was the same as with the Zeiss microscope we used before.

The organic shell around the nanoparticles is always a big problem for SEM imaging, as an excessive accumulation of this material produces charging effects. Furthermore, the organic layer generates an additional electron signal (SE), which makes high resolution imaging due to the appearing luting effect impossible. The new SEM is equipped with a retractable low-voltage high-contrast solid state detector (vCD) for backscattered electrons [104]. Only the higher energetic electrons from deeper layers trigger this detector and one gets more information of the structure below the organic material (see figure 3.2). The additional SE electrons from the upper organic layer are not disturbing the signal in this case. The black areas in the middle of the particle faces (looking like holes in the structure) in figure 3.2b are a result of long, tube-like voids present in the bct structure, where the empty planes between particle faces of subsequent layers intersect so that no particle is present in any of the subsequent layers. If the organic layer was too thick and the sample was not to be characterized magnetically afterwards, an oxygen plasma was applied to remove the organic surface layer. The plasma generator was operated for one hour to remove a few atomic layers. The success of this treatment is shown in figure 3.3, where the difference due to the plasma treatment is clearly visible.

### 3.3 Transmission electron microscopy

Transmission Electron Microscopy (TEM) studies were used to reveal essential information about the morphology of the single nanoparticle, stacking of nanoparticles layers and the presence of stacking defects and/or dislocations in the mesocrystals. In TEM, a highly coherent electron beam passes through a thin, electron transparent specimen. The transmitted electron beam can be used to record images (real space) or diffraction patterns (reciprocal space). The TEM characterization was done on cross-sectional specimens that were prepared by Focused Ion Beam (FIB) (see section 7.1). Different TEM images and diffraction patterns are recorded using a 2k x 2k CCD camera. The TEM studies were performed in collaboration with Andras Kovacs from the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Peter Grünberg Institute 5, Forschungszentrum Jülich.

The shape, size and atomic crystal structure of individual nanoparticles was investigated using aberration-corrected High-Resolution TEM (HRTEM). The specimens are prepared from drop
3.4 Atomic force microscopy

Atomic Force Microscopy (AFM) was used as a complementary surface sensitive technique. A thin tip, sitting on a flexible cantilever, is used as a measuring sensor to scan over the sample surface. In this work, all AFM images were obtained in a standard AC mode (non-contact),
Chapter 3 Experimental Methods

Figure 3.5: Example pictures for a height profile in different magnifications measured with an AFM in non contact mode.

where the tip does not touch the sample surface. In this mode the cantilever is oscillating near the resonance frequency and is scanned over the sample. The changing cantilever amplitude and phase due to the modification of the interaction between specimen and tip is recorded, while keeping the distance constant via a feedback loop. The topography of the specimen investigated is constructed from the necessary readjustment to reach a constant amplitude of the cantilever’s oscillation.

This method was used to obtain the height profile of the samples as well as an independent check of the lateral size of the mesocrystals grown, an estimate of their shape and the mesocrystal density on the substrate in comparison to the SEM. An example of a height profile measured with AFM is shown in figure 3.5a. The advantage of measuring the height of mesocrystals by AFM is that these datasets contain information in three dimensions. The relative height of the sample surface is measured at every position (x,y) in dependence on the position of the raster. So a more quantitative determination of the height of single mesocrystals is possible, in comparison to the SEM where only a two dimensional image is obtained.

For this study an Agilent 5400 scanning probe instrument was used [101]. The organic shell around the particles does not allow a contact mode due to the high probability of snagging organic material on the tip. The additional material leads to an overshoot and makes measurements impossible. Furthermore it could happen that a nanoparticle is graped with the tip and moved [54]. The mesocrystal samples implicate a slow scan speed to avoid contact and edge artefacts, due to the large difference in height of up to 800 nm and the large scanning area. The possible lateral resolution is mainly determined by tip shape and size. For a higher resolution a sharper tip is required. In this work a cantilever with ≈4 nm tip size is used at ≈250 kHz, which allows a lateral resolution of approximately 10 nm. The difficulty to resolve the order of the nanoparticle stacking on top of a mesocrystal is increased by the organic material, which lies in the void between the particles and masks the structure of the individual particles. Additionally it is known that the AFM tip follows the height variations on a hard surface with higher fidelity than on soft areas [100]. But despite all these difficulties, it was possible to resolve the nanoparticle structure in rare cases (see figure 3.5b). The inset shows the Fourier transformation of
the topography image and the presence of long-range order with sharp peaks. The coherence in the vertical direction is lower, as the tip was scanned in horizontal direction. The PicoView instrument software was used to apply leveling, polynomial form removal and line correction to the images to remove sample tilt, non-linearity effects of the piezo drives and electronic noise from the images, respectively.

3.5 X-ray reflectometry

A Bruker AXS D8 X-Ray Reflectometer (XRR) was used to investigate the structural correlation along the direction of the surface normal in the nm range with high intensity. In-plane correlations can only be resolved in the μm range. The Göbel mirror monochromator parallelizes the Cu Kα radiation generated from a sealed tube X-ray source (see figure 3.6). The first two slits define the beamsize and reduce the background. A switchable attenuator is installed between these slits, to reduce the intensity to avoid over illumination of the detector. The sample table has motors for z translation and the χ angle. Another Göbel mirror is mounted on the detector arm to focus the scattered beam onto the last slit, which is responsible for the angular resolution. The slits were chosen to achieve a beam size between 0.2 and 0.4 mm. The used detector is a NaI scintillator. The setup allows measurements in specular and off-specular scattering geometries and up to a 2θ angle of about 110° in the specular case. The X-ray reflectometer was used for a first fast evaluation of the nanoparticle stacking in c direction (perpendicular to the substrate) averaging over the sample. Only a few minutes are needed to get a reflectometry curve with good statistics. The existence of strong Bragg peaks indicate a good order along the c direction. The average interparticle distances perpendicular to the substrate can be deduced from the distance of the peaks. Additionally, a clear distinction between monolayer, multilayer or an ensemble of mesocrystals can be done. Due to the possibility of accessing the atomic scale at large angles, a first evaluation of the atomic crystal structure of
the single nanoparticles and their preferred orientation inside the mesocrystals was possible as well. A sketch of the principle design of the instrument is shown in figure 3.6.

3.6 Small angle X-ray scattering

The morphology of the nanoparticles in solution was investigated with a Bruker AXS Nanostar® laboratory Small Angle X-Ray Scattering (SAXS) instrument [102]. The extracted particle size distribution and the average radius of the nanoparticles in the solution are important precharacterizations for the process of self-assembly and further investigations. The sample solutions were filled into quartz capillaries with an inner diameter of 1.5 mm and a wall thickness of 0.01 mm.

The SAXS measurements were performed with Cu K$_\alpha$ radiation (1.54 Å wavelength), produced by a rotating anode source operated at 40 kV, 40 mA with a double Göbel mirror monochromator. A pin-hole collimation system defines a precise x-ray beam which hits the sample inserted in a multi-sample holder. This holder is mounted on an yz-stage in a vacuum chamber. Scattered from the sample, the beam hits a 2-dimensional VANTEC 2000 xenon gas filled detector with 2048x2048 pixels on a 14x14 cm$^2$ area. The distance between sample and detector is fixed at 1.07 m. The accessible Q-range was defined by the primary beamstop of 2 mm diameter positioned at a distance of 1.05 m from the sample and the detector size to 0.007 - 0.25 Å$^{-1}$. A sketch of the instrument design is shown in figure 3.7.

3.7 Grazing incidence small angle X-ray scattering

Grazing Incidence Small Angle X-ray Scattering (GISAXS) was used to determine the 3 dimensional structure of the assemblies in the nm range. While the reflectometer has only a nm resolution in the out-of-plane direction, GISAXS provides access to both directions resolving the nanometer scaled structure of the ensemble of mesocrystals. The subtleties of the in-plane
ordering can be visualized and a full quantitative interpretation can be made by extracting the space group as well as the coherence length, lattice constant size and distribution and tilting angle. The sample properties and the measured intensity pattern resulting from them, are an average over a large sample area, that is illuminated by the beam (footprint). In this measurement geometry, the ensemble of mesocrystals can be investigated as grown on the substrate without cutting the sample.

The general setup of a GISAXS experiment is shown in **Figure 3.8**. The X-rays from the source are guided through a vacuum system to the sample by the use of various lenses and mirrors, monochromators and slits to achieve a monochromatic and sufficiently collimated/focused beam. The beam size can be influenced by the last set of slits in front of the sample position. Together with the detector resolution and distance these optics define the experimental resolution. The beamsize at the sample position is of importance, as it controls the footprint on the sample and thus the scattering area. The X-rays hit the sample under a small angle of incident (usually 0.1 - 0.5°). A 2-dimensional detector records the scattered intensity pattern as in the SAXS experiments, but with a higher detector position to access more of the upper hemisphere above the sample horizon. Typically, three translation and two inclination motors are installed to align the sample and change the angle of incidence. The Q range can not only be changed by the choice of the energy but as well by variation of the distance between sample and detector. A GISAXS beamline can be used for SAXS measurements as well if it is equipped with the appropriate beamstop. For both experiments the central area around the direct beam needs to be shadowed, especially for alignment when the unattenuated beam can hit the detector. The strong specularly reflected beam in GISAXS experiments necessitates the full coverage of the specular line to avoid detector damage or saturation effects, so a long, rectangular shaped beamstop is needed in addition (only for synchrotron setups).

The configuration of a GISAXS setup varies from beamline to beamline, the measurements presented in this thesis were obtained at the following instruments:

- **The SWING beamline at the synchrotron Soleil, Gif sur Yvette, France** [112] was
used to measure GISAXS for structural characterization of dried samples where the influence of different self-assembly parameters was investigated. An in-vacuum U20 undulator provides an incident energy of 7 keV. A beam focus of 40x400 µm was used. We fixed our dedicated vacuum sample holder on a standard micro control holder to have an available sample size of up to 5 cm in diameter. In this configuration, a z translation adjusts the sample to the center of the beam and a θ-cradle changes the incidence angle. The detector is a stack of 2x2 Aviex CCD detectors with 2048x2048 pixels each in a distance of 0.91 m to the sample position. Software binning of 4x4 pixels is applied to reach a final resolution of 1024x1024 pixels of 165x165 µm² size. The detector position was off-centered to allow the measurement with a maximum Q of 0.6 Å⁻¹. For the GISAXS measurements the angle of incidence was varied from 0.1 to 1.0°. The exposure time used was 0.5 s per image.

- The ID01 beamline at the Synchrotron ESRF, Grenoble, France [111] was used for the real time monitoring of the mesocrystal growth by in-situ SAXS and GISAXS (see chapter 6). The synchrotron light from the 3rd generation source is produced by an undulator, which was set to the 9.8 keV incidence energy, well above the Fe K-edge at 7.112 keV. This was a compromise to be high enough above the absorption edge while staying in the detector sensitivity range. The focusing of the beam to 25x1000 µm was done with a lens, to achieve a stable beam with small footprint. Our self developed sample setup (see section 6.1) was mounted on a Huber Tower with xyz-translation and θ χ rotation stage. A Princeton CCD detector with 1242 x 1151 pixels and a pixel size of 54x54 µm² was set at a distance of 1 m from the sample. In this configuration the available Q-range was ± 0.16 Å⁻¹. The CCD was coupled to a fast shutter system, so that the sample and CCD were only exposed during acquisition. This is necessary for a correct readout of the CCD and protects the sample from radiation damage. The acquisition time of 1 s and a readout time of 7 s defined our time resolution.

- The laboratory GISAXS setup at the Technical University of Denmark, Risø Campus, was used to characterize the mesocrystal structure of other dried samples. The measurements were performed using Cu Kα radiation from a rotating anode operated in fine focus mode, monochromatized and focused by a single reflection graded multilayer optics and further collimated by 3 pinholes. The entire beam path is evacuated to prevent air scattering. Two translations and a rotation are available to align the sample. A two dimensional delay line gas detector [44] with a sample-to-detector distance of 1.435 m allows a Q-range of 0.01-0.35 Å⁻¹. A 4 mm diameter circular SAXS beam stop was positioned directly in front of the detector and thus the specular line was measurable, too. Such a measurement is possible at this instrument without destroying the detector because of the lower incident intensity compared to a synchrotron source and by selecting an angle of incidence above the critical angle of total reflection. This way it is possible to measure the specular line in the GISAXS pattern, as well. The exposure time was obviously much longer than at a synchrotron (10-30 minutes).

3.8 X-ray diffraction

X-Ray Diffraction (XRD) is the traditional method to investigate the atomic structure and orientation of crystals. An Eulerian cradle with a large angular range is a standard part of a four circle
3.8 X-ray diffraction

or a six circle diffractometer. In this work we used two kinds of diffraction studies, wide angle crystal diffraction on a laboratory 4-circle diffractometer and small angle single mesocrystal measurements on a synchrotron source.

The investigation of preferred orientations of the nanoparticle crystalline lattice inside the mesocrystals was performed at our Huber 4-circle diffractometer equipped with a Cu K$\alpha$ sealed tube X-ray source and a double Göbel mirror monochromator to monochromatize and parallelize the beam. The collimator, which only confines the beamsize, was not used to get more flux on the sample. The beam size was about 2x2 mm$^2$. The detector arm has slits to define the resolution at the detector and the scattering pattern is recorded by a NaI scintillation detector. The 4-circle diffractometer allows a higher degree of freedom than the D8 instrument because of its 4 angles ($\omega$, $2\Theta$, $\phi$, $\chi$). For $\chi = 90^\circ$ and $\phi = 0^\circ$, a normal $\omega/2\Theta$-scan geometry is achieved. Other $\phi$ and $\chi$ values allow to reach any Q-position with $Q_z > 0$ in reflection geometry. Additionally, an xyz translation stage is installed for alignment purposes. For approaching the different (hkl) values, the SPEC instrument software is used to calculate the angles from the lattice information of $\gamma$-Fe$_2$O$_3$ given in [72]. While the D8 reflectometer (see section 3.5) gives only the out-of-plane information about a preferred orientation with higher intensities, a 4-circle diffraction experiment enabled us to characterize peaks in any direction.

At the high resolution diffraction beamline P08 of the synchrotron radiation source PETRA III at DESY in Hamburg [80], small angle diffraction studies have been carried out to investigate the structure of single mesocrystals (see chapter 7). To be able to investigate crystals of $\mu$m size some requirements are absolutely mandatory: The x-rays have to be focused down to the size of the crystal to achieve high photon flux densities, the beam position has to be stable within a fraction of the sample diameter, the background has to be virtually zero and the motor resolution has to be significantly better than the sample size and the width of the Bragg

Figure 3.9: Setup for a diffraction experiment- here the inhouse 4circle diffractometer.
To achieve focusing with a spot size of 5 µm vertically and 10 µm horizontally, sets of compound refractive lenses [59] have been utilized. The photon energy of 12.4 keV provides a high integrated flux ($10^{11}$ photons/second at the sample) and is sufficiently far away from the iron K-edge at 7.1 keV, avoiding high background due to x-ray fluorescence. The detector of choice was a Princeton Instruments Quad-RO 4096 CCD with 4096x4096 pixels at a pixel size of 15x15 µm$^2$, mounted 0.77 m from the sample. This detector has a very good efficiency at 12.4 keV. To reduce the background scattering an evacuated pipe was installed between sample and CCD.

The experiment was done in a typical SAXS geometry in transmission (see figure 3.7) but with additional rotational degrees of freedom (see figure 3.9). This figure also holds for this setup, because we only used 4 degrees of the 6-circle diffractometer.) to enable high resolution diffraction analysis similar to that for atomic crystals, but now on the length scale of nanometers. To translate the sample into the beam an xyz-stage was used, to orient it a double goniometer on top of this stage. After full spatial and orientational alignment, sample-tilt ($\omega$) and sample-azimuth ($\phi$) angles have been scanned to take the diffraction patterns. The resolution in Q-space is basically determined by the pixel size of the detector and the divergence of the beam. The energy resolution $\delta E/E$ was $0.5 \cdot 10^{-4}$.

### 3.9 Space group evaluation of GISAXS data

The analysis of the space group is done according to well established crystallographic methods [7, 11], but with the special case that all reflections hkl from different directions arise in one single GISAXS pattern without any rotation of the sample, as in a powder sample, but with additional directional information for the out-of-plane axis. In other words, the 2D powder leads to reciprocal space rings in the $Q_x$-$Q_y$ plane and the experiment measures one slice through this plane. The pure (00l) reflections have a ring radius of 0 and therefore lead to much stronger reflections in the measured plane. The flat Ewald sphere in small angle scattering, as well as the 2D powder property with the in-plane orientation average induce this phenomenon. The structural symmetries and inter-particle correlations are described by the structure factor (SF) (see section 5.1.1) consisting of the nanoparticle and mesocrystal form factor (FF) convoluted with the unit cell Fourier transform times the reciprocal lattice. In comparison to atomic crystals the nanoparticle FF complicates the analysis as several FF minima lie in the observed Q-range and can lead to additional extinction of reflections allowed by the selection rules. Dividing by the corresponding FF leads to equalized intensity for the peaks. Division by zero is avoided in this process, as the formfactor always contains a size distribution, leading to non zero values over the whole Q-range. The $Q_z$ direction of the GISAXS pattern contain information of the correlations perpendicular to the substrate, while $Q_y$ exhibits in plane nanoparticle correlations, with a component in $a^*$ or the combination of $a^*$ and $b^*$ as reciprocal lattice vectors. In our case of simple unit cell structure, the first peak in $Q_y$ direction gives the reciprocal lattice constant $a^*$ and the smallest distance between any two reflections in $Q_z$ direction, measured at higher Q values to eliminate refraction, is the reciprocal lattice constant $c^*$ in c direction of the crystal (out-of plane of the substrate). Using this procedure one has to check if a second structure or superstructure exists. If this is the case the structures have to be separated and the same treatment can be used. Indexing of the peak is done by taking multiples of the reciprocal lattice...
3.9 Space group evaluation of GISAXS data

constants (a* and c*). The existing peaks and the extinguished reflections yields the selections rules, which lead to the possible space groups.
Chapter 4

Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

Fundamental research on nanocrystals and self-assembled nanostructures is a major part of today’s scientific effort for the design of novel materials [46, 94]. A reproducible production of highly ordered nanoparticle systems is an important step for its further development. The process of self-assembly is a promising way for the fabrication as it allows mass production processes of very small structures over a large area without the use of expensive equipment. The physical process itself is complex, including several interactions between nanoparticles, solvent and substrate [83]. Understanding and optimizing the arrangement of nanoparticles in structures like supercrystals or superlattices at all length scales is an important step towards controlled design.

If the resulting superstructures are μm sized discrete islands of three dimensionally highly ordered particles they are called mesocrystals. This chapter will provide the post deposition properties of the self-assembled structures observed after different deposition conditions and herefrom deduce the properties of the self-assembly process. The gathered knowledge was used to improve the self-organization procedures and tune the resulting parameters of the sample.

Basic requirement for an optimal self-assembly process is the quality of the nanoparticles, especially the size distribution. An overview of the results of the atomic order, magnetic and morphological precharacterization of the single γ-Fe$_2$O$_3$ nanoparticles is summarized. Here, the focus is in the morphological characterization including particle size and size distribution.

The main point of this chapter is the preparation and the three dimensional structural characterization of highly ordered assemblies of iron oxide nanospheres and nanocubes. A short overview of the known mechanisms of self-assembly is given and discussed with respect to the system used. The structural characteristics of the assemblies are introduced and analyzed with the application of several complementary methods for a good overview. The influences of the preparation conditions on the resulting structures have been studied, allowing to optimize and selectively influence the system. Under extraordinary conditions completely different macroscopic structures can evolve. Preferred directions of the single nanocrystals inside the mesocrystals may lead to a change of the overall magnetic behavior due to the aligned anisotropy axis. These aspects are also discussed in the present chapter.
4.1 \(\gamma\)-Fe\(_2\)O\(_3\) nanoparticles

This section provides an introductory description of the \(\gamma\)-Fe\(_2\)O\(_3\) nanocrystals used, showing the good quality of the samples as revealed by the morphological characterization including particle size and size distribution.

4.1.1 Preparation

Spherical and cubic particles were used for the investigations described in this work. The samples in the form of pastes or solutions were obtained through a collaboration with Prof. L. Bergström and his group from Stockholm University, Sweden. The synthesis of the nanoparticles [14] is a modification of the nonhydrolytic thermal decomposition of iron-oleate in an high-boiling organic solvent [68]. The following information about the particle fabrication was provided in a private communication with German Salazar Alvarez and Erik Wetterskog from the mentioned group.

The iron-oleate complex was prepared following a procedure similar to what has been previously reported [14]: 10.8 g of iron chloride (FeCl\(_3\) \cdot 6H\(_2\)O, 40 mmol, Aldrich, 98 %) were refluxed with 36.5 g of sodium oleate (120 mmol, Sigma, 82 %) in a solvent mixture of 140 cm\(^3\) hexane, 80 cm\(^3\) ethanol and 60 cm\(^3\) distilled water at 70 °C for 4 hours. The organic phase was washed three times in 30 cm\(^3\) of distilled water prior to the removal of hexane using a rotary evaporator. A dark brown iron-oleate residue is achieved from this process.

The synthesis was performed in a solution of 36 g of the iron (III) oleate (40 mmol) and 200 cm\(^3\) 1-octadecene (Aldrich, 90%) degassed under vacuum at 80 °C for 1 hour to remove water prior to the addition of oleic acid and increasing the temperature up to the reflux temperature of 320 °C. The synthesis process by thermal decomposition of iron-oleate in an high-boiling organic solvent allows a perfect control of nanoparticle size and size distribution due to the separation of the nucleation and growth kinetics, which result from the separate temperature dependence of the processes [68]. Nucleation centers are produced through a decomposition of the iron oleate by heating up the precursor solution slowly through the nucleation temperature range of 200-240 °C to higher temperatures. The slow increase of the temperature enables the nucleation process to finish before the growth process starts. The growth rate of the particles accelerates above 300 °C and is temperature dependent. To reach smaller nanoparticles, a lower boiling solvent and shorter heating time at the boiling point is necessary. The additional amount of oleic acid during the synthesis influences the particle size, too. In the case of the particles used the shapes were controlled by the amount of additional oleic acid (the iron-oleate:oleic acid molar ratio) and the heating rate [14]. The small decrease of the heating rate from 3 °C/s to < 2.6 °C/s together with a lower additional amount of oleic acid supports the production of nonspherical nanocrystals. For the synthesis of nanospheres, 5.7 g (20 mmol) of oleic acid was added and a regular reflux apparatus setup was used and heated up with 3 °C/min up to 320 °C, whereas for the synthesis of nanocubes, a Dean-Stark condenser was incorporated, the solution was heated up at 2.6 °C/min to 320 °C and 3.2 g (11.3 mmol) of oleic acid was needed. Both mixtures were refluxed for 30 min under N\(_2\) after which the vessel was allowed to cool down.

The nanoparticles were separated by centrifugation through several precipitation cycles using a solvent/non-solvent pair (n-heptane/ethanol) resulting in a concentrated paste. At the end
Table 4.1: Produced nanoparticle solutions which were used.

<table>
<thead>
<tr>
<th>Solution ID</th>
<th>shape</th>
<th>concentration</th>
<th>solid content in paste (from TGA)</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{0.1}</td>
<td>spherical</td>
<td>0.1 \cdot 10^{14} NP/ml</td>
<td>61 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{0.1}</td>
<td>cubic</td>
<td>0.1 \cdot 10^{14} NP/ml</td>
<td>43.5 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{1.0}</td>
<td>spherical</td>
<td>1.0 \cdot 10^{14} NP/ml</td>
<td>61 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{1.0}</td>
<td>cubic</td>
<td>1.0 \cdot 10^{14} NP/ml</td>
<td>43.5 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{4.7}</td>
<td>spherical</td>
<td>4.7 \cdot 10^{14} NP/ml</td>
<td>61 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{4.7}</td>
<td>cubic</td>
<td>4.7 \cdot 10^{14} NP/ml</td>
<td>43.5 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{8.4}</td>
<td>spherical</td>
<td>8.4 \cdot 10^{14} NP/ml</td>
<td>61 wt%</td>
<td>toluene</td>
</tr>
<tr>
<td>S_{8.4}</td>
<td>cubic</td>
<td>8.4 \cdot 10^{14} NP/ml</td>
<td>43.5 wt%</td>
<td>toluene</td>
</tr>
</tbody>
</table>

a black nanoparticle paste is achieved with 61 wt% iron oxide for the spheres and 43.5 wt% iron oxides for the cubes. The fraction of inorganic content of this paste was estimated from the residual mass after heating to 800 °C in air employing a Perkin Elmer Thermogravimetric Analyzer TGA-7 at a heating rate of 10 °C/min.

The dispersions were produced by diluting the paste in toluene in a ratio determined from the iron oxide content to achieve the desired particle concentrations. For a nicely dispersed solution, manual shaking and subsequently sonication for 15 minutes is applied to produce stable solutions. The solutions used and their sample IDs are listed in table 4.1. The capital S is the symbol for solution, the subscript character for the shape (S:spherical, C:cubic) and the superscript the concentration. These sample ID’s will be used for the identification of the nanoparticle solutions in the subsequent chapters.

4.1.2 Structural characterization

The structural characterization of the nanoparticles inside the solution is an important prerequisite to understand the results of the investigations of the ordered particle assemblies. In addition to the characterization done in this work, an extensive collection of results published in the PhD thesis of S. Disch [103] is available.

Structure on the atomic scale

The nanoparticles used consist of an inorganic core covered with an organic shell. The atomic structure of the inorganic core is crystalline and shows an inverse spinel structure with $a = b = c = 8.36$ Å and a Fd$ar{3}$m space group having 8 formula units, which was confirmed by x-ray diffraction [52, 103]. The distinction between magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$) could be made using the occupancy of the iron sites, deduced by Mössbauer spectroscopy and the atomic pair distribution function. From this analysis predominantly maghemite was found [52], suggesting a core shell structure consisting of a magnetite core (less than 5-10%) and a maghemite shell [103].

Morphological characterization

The extraction of the particle size distribution and the average radius of the nanoparticles is an important pre-characterization for the self-assembly and all further investigations. This study was done in this work with small angle X-ray scattering at an in-house lab source (section
Chapter 4 Fabrication and properties of \(\gamma\)-Fe\(_2\)O\(_3\) nanoparticle assemblies

<table>
<thead>
<tr>
<th>Solution ID</th>
<th>model</th>
<th>radius (r_{\text{NP}})</th>
<th>edge length (a_{\text{NP}})</th>
<th>size distribution (\sigma)</th>
<th>degree of truncation (\tau)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_0^{0.1}:) spherical FF</td>
<td>(5.01 \pm 0.02) nm</td>
<td>/</td>
<td>(6.3 \pm 0.5%)</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>truncated cube FF</td>
<td>/</td>
<td>(10.02 \pm 0.04) nm</td>
<td>(5.6 \pm 0.6%)</td>
<td>0.94 (\pm 0.05)</td>
<td>/</td>
</tr>
<tr>
<td>(S_0^{0.1}:) rounded cube FF</td>
<td>/</td>
<td>(10.90 \pm 0.04) nm</td>
<td>(5.8 \pm 0.5%)</td>
<td>0.80 (\pm 0.05)</td>
<td>/</td>
</tr>
<tr>
<td>spherical FF</td>
<td>(6.04 \pm 0.02) nm</td>
<td>/</td>
<td>(5.6 \pm 0.4%)</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.2: Results of the SAXS analysis for the morphological characterization of spherical and cubic \(\gamma\)-Fe\(_2\)O\(_3\) particles. The data for the cubes were fitted with different form factor (FF) models as comparison. The description of the models can be found in section 5.1.1. The errors are estimated from the fitting procedure.

3.6). SAXS investigations give only structural information about the inorganic nanoparticle core due to the small contrast between the nanoparticle shell and the organic solvent. X-rays mainly probe differences in electron density, which is very similar for the oleic acid ligand and the matrix of toluene. The determination of the organic shell thickness is only possible with a SANS measurement, which was done by S. Disch [103]. With neutrons, a strong nuclear contrast between non-deuterated oleic acid and deuterated toluene can be used to be able to determine the shell thickness.

The nanoparticle dispersions \(S_0^{0.1}\) and \(S_{0.1}^{0.1}\) were diluted from higher concentration for this experiment to have enough scattering centers, but not to be too dense to produce too much absorption or to create a structure factor. The solution was poured into Hilgenberg borosilicate glass capillaries with an outside diameter of 1.5 mm and a wall thickness of 0.01 mm. The capillaries were sealed by melting the glass with a torch. The raw datasets were time-normalized and corrected for the detector sensitivity, empty cell scattering and dark current. The I(Q) scattering curves were determined by radially averaging over the corrected data. In addition, the dataset was normalized to absolute units by the use of a reference material. The resulting S(Q) plots are shown in figure 4.1 and figure 4.2.

The results listed in table 4.2 were extracted by fitting the data with the corresponding form factor (FF). The instrumental resolution is taken into account to achieve a good refinement of the model to the data and to avoid a masking of the narrow size distribution due to limited instrument resolution. The small structure factor contribution for the \(S_{0.1}^{0.1}\) solution in the lower Q-range is negligible, as the data above 0.05 Å can be perfectly fitted with a pure form factor. Small agglomerations and/or a too large density in the solution can generate such a structure factor. In this case the refinement was done in the Q-range where the structure factor contribution could be neglected.

The depth of the minima already indicate a very narrow particle size distribution. In this case the log-norm size distribution of the model (\(\sigma_{\text{aNP}}, \sigma_{\text{rNP}}\)) certifies a narrow distribution around 6 \(\pm 0.5\%\) for both solutions, which is in agreement with earlier studies [34, 103]. These monodisperse nanoparticle solutions are an important pre-condition to achieve a well ordered assembly of particles [99] and to have magnetic characteristics homogeneously over the solution, due to the size dependent blocking temperature [107, 108].

The information about the average size of the inorganic nanoparticle cores in the solution is contained in the position of the minima of the oscillations. Larger particles will lead to a shift of the minima positions to lower Q values. The refinement of the \(S_0^{0.1}\) solution with a spherical FF shows a perfect agreement (figure 4.1) and yields an average radius \(r_{\text{NP}}\) of 5.01 \(\pm 0.02\) nm.
4.1 $\gamma$-Fe$_2$O$_3$ nanoparticles

**Figure 4.1:** SAXS from spherical particles $S'_S$ fitted with a spherical FF. The fit parameters are shown in table 4.2.

**Figure 4.2:** SAXS from cubic nanoparticles $S'_C$ fitted with a spherical, truncated cubes and rounded cubes form factor. The fit parameters are shown in table 4.2.
Chapter 4 Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

Figure 4.3: TEM pictures of the used particles, deposited on a TEM grid.

of the particles. TEM pictures of single spherical particles with different magnifications are presented in figures 4.3a, 4.3b and confirm the spherical shape and narrow size distribution. The determination of the organic shell by S.Disch shows a shell thickness of 1-2 nm [33, 35, 103] and has to be considered for the distance between two nanoparticles in the assemblies described later.

The SAXS data from the cubic nanoparticles $S_C^{0.1}$ were fitted with a truncated cubical [33], a spherical [71] and the newly developed rounded cubical FF (equation 5.5, figure 5.1). All are shown in figure 4.2. The best refinement of the truncated cube model does not fit the data at all minima and shows that this morphological model with flat facets is not describing these particles very well. The model of highly truncated rounded cubes and the spherical FF fit the scattering curve much better, but the data is insufficient to distinguish between the two models. Small differences in the shape could be visible with a larger Q-range, which could however, not be accessed with the lab-source instrument due to the low intensity. The TEM pictures with high resolution show clearly a cubic shape characteristic with rounded edges (figure 4.3d). The result of the form factor modeling yields a non-spherical nanoparticle with an edge length $a_{NP}$ of 10.90 ± 0.04 nm and an degree of truncation $\tau_{Round}$ of 0.8 ± 0.05. It should be noted that these results are an average over all particles in the solution.

4.2 Self-assembly of 3D ordered nanoparticles

This section will focus on the preparation and characterization of highly ordered 3D nanoparticle assemblies of iron oxide nanospheres and nanocubes. The nanoparticle superstructures developed are single crystals consisting of nanoparticles and are called supercrystals or (in this thesis) mainly mesocrystals. A further step of understanding and optimizing the process of mesocrystal growth is one main goal.

4.2.1 Sample preparation

For the preparation of highly ordered 3D supercrystals of different nanoparticle shapes, a drop casting method is used to generate a drying-induced self-assembly. A substrate is covered with the nanoparticle suspension, and during the evaporation of the solvent in a controlled
atmosphere and under an applied magnetic field the nanoparticles arrange in ordered structures. The physical process itself is complex, including several interactions between nanoparticles, solvent and substrate. A more detailed description of the self-assembly mechanism is given in chapter 6. The drop casting method allows us to produce an ensemble of mesocrystals over a 2" substrate homogeneously. Details about the exact preparation technique are summarized in the following paragraphs.

Substrate and substrate cleaning
As substrates, silicon wafers with a thickness of \(525 \pm 25\ \mu m\), N/Phosphor doping and a \(\langle100\rangle\) orientation from the Si-Mat company are used. Depending on the requirements of the experiments, samples from \(5\times5\ \text{mm}^2\) to 2" size were produced. Before the drop casting, the substrates are cleaned by sonication in ethyl acetate and ethanol for 30 min each. Afterwards they were stored in an ethanol bath until use. Before the usage the substrates were dried with compressed \(\text{N}_2\) to prevent from dust trapping.

Evaporation chamber
The self assembly takes place in a closed petri dish or the customized in-situ cell (section 6.1). Both chambers have the possibility to control the evaporation rate with a well-defined amount of toluene in a dedicated reservoir inside the evaporation chamber. The in-situ cell has additional outlets to control the gas exchange between the chamber and the surrounding atmosphere. The setups allow a time for complete evaporation of the solvent between a few minutes and several days, which could be reached using the open chamber with no reservoir, or the closed chamber by saturating the atmosphere before the drop casting and using 400 \(\mu l\) toluene as reservoir. To produce a well ordered assembly of mesocrystals with a defined shape, longer evaporation times are needed (see section 4.2.4.3).

Deposition
The substrate surface is aligned horizontally using an adjustable table and a spirit level. The Si-substrates are then covered with a nanoparticle solution in toluene with a concentration of \(8.4\times10^{14}\ \text{NP/ml} (S_8^{8.4} \text{ and } S_8^{8.4})\) for mesocrystal growth and \(1.0\times10^{14}\ \text{NP/ml} (S_8^{1.0} \text{ and } S_L^{1.0})\) as base suspension to produce dilute solutions for monolayer growth. A typical deposition is made by applying a 20 \(\mu l\) droplet per cm\(^2\) on the cleaned wafer.

Magnetic field
For most samples a defined magnetic field was applied during the process of self assembly. For the optimization of this process, the influence of the magnetic field direction and strength on the mesocrystal growth was investigated (see section 4.2.4.2). For this study, magnetic fields with field gradient pointing away from the sample surface \(H_{\perp}\) (gradient up), pointing towards the sample surface \(H_{\parallel}\) (gradient down) and pointing along the substrate \(H_{\parallel}\) (gradient in-plane), as well as a homogeneous field in the in-plane \(H_{\parallel}\) (in-plane homogeneous), the out-of-plane direction \(H_{\parallel}\) (homogeneous) and with zero field were applied (see figure 4.4). The strength of the magnetic fields reached from a few mT to 100 mT at the sample position with a
gradient between $10^{-1}$ and $10^{2}$ mT/cm. The magnetic fields were accomplished either by a coil especially for the 2 inch samples or a permanent magnet with a smaller area but higher field strength and gradient. The fields were applied during the entire drying processes.

Sample IDs
The self-assembled samples will be referred in the following by:

$$D_{\text{time, particle surface density, gradient direction and field strength}}$$

at which D denotes a drop-casted sample. The shape denotes one of S for spherical and C for cubic particles. The size of the particle is given in nm, at which the number indicates a radius for spherical and an edge length for cubic nanoparticles. The degree of truncation is only given for the cubes. The time was varied between short (SH), which was a few minutes, medium (MD), meaning a few hours and long (LG), where the droplet evaporation needs days. The particle surface density deposited on the substrate is given in $10^{6}$ NP/mm$^2$ and was calculated from the particle density in the solution, the deposited amount and the substrate surface area (e.g. $1.86 \times 10^{6}$ NP/mm$^2$ $\cong$ a concentration of $8.4 \times 10^{14}$NP/ml, an amount of $20 \mu$l solution and 1 cm$^2$ surface area). The symbols for the gradient directions are used as defined in the paragraph above and the value of the field strength is given in mT. The used sample ID gives all necessary information about the parameters of the self-assembly and will be used in the subsequent chapters.

Reproducibility
In this PhD work, all $\approx$ 300 samples showed formation of mesocrystals. The reproducibility of the mesocrystal growth could be guaranteed by continued use of the same process and the respective parameters. The same solutions with constant concentration, equivalently treated substrates and precisely defined amounts of solution per surface were used. Thus it was possible to reach the same number of particles per cm$^2$. The same conditions on the substrate surface lead to the same droplet wetting behavior, which again can influence the self-assembly process. The reproducible order of magnitude of evaporation speed is an important factor for the self-assembly due to the time available for the ordering and could be verified using the light-band micrometer (section 6.1). Especially the in-situ cell enables perfectly reproducible conditions for the control of the growth parameters.
Mesocrystal samples produced with the same parameters show similar characteristics (compare figure 4.5a and figure 4.5b). Nearly the same surface coverage, equivalent mesocrystal shapes and sizes are observed.

### 4.2.2 Model for the mesocrystal growth

The 3D supercrystals are produced by an evaporation induced self-assembly on a substrate. In general, self-assembly is understood as autonomous ordering of preexisting components into more complex structures without external intervention [94]. Autonomous ordering means an organization induced by specific interactions between the components themselves. Model concepts of the mesocrystal growth will be discussed in this section to explain the process and its outcome.

The substrates are covered with nanoparticle dispersions consisting of $\gamma$-Fe$_2$O$_3$ nanoparticles with oleic acid as ligand dissolved in toluene. The entire substrate surface is wetted with a droplet (see figure 4.6a), even for 2" wafers. The nanoparticles are freely movable in the solution by Brownian motion. During the controlled evaporation of the toluene the droplet shrinks, the contact line between the substrate and the end of the droplet stays pinned (see section 6.3 stage 1) and the particle density of the solution increases, yielding less free space for the nanoparticle motion. The process of self-assembly is not induced before a critical concentration is reached which is defined by the length scale and magnitude of the required interactions [24].

The short mean free path of the particles increases the probability of the formation of stable clusters [24] (section 2.1.5) which act as nucleation centers for the growth of mesocrystals. The necessity of a critical concentration is experimentally shown in section 6.3.

The process of self-assembly is governed by the interaction of different attractive and repulsive forces. As described by Bishop et al. [24], van der Waals, electrostatic, magnetic and entropic forces are the fundamental interactions between nanoparticles and can be used to tune the nanoscale self-assembly. For our system the van der Waals and dipole-dipole attraction, as well as a steric repulsion make up the total interaction potential.

The self-assembly of sufficiently small particles into ordered states is mainly induced by the attractive van der Waals force [24, 33, 58, 99]. The electrostatic repulsive interaction forces, due to overlap of electron orbitals of the outer atomic shell, provide the balancing force to create stable structures [14, 24, 99]. The application of a medium strength magnetic field during the self-assembly induces a stronger dipole-dipole attraction in super paramagnetic particles, but has minor influence on the self-assembly itself. This could be shown experimentally in section 4.2.4.2, where in absence of an external magnetic field equally highly ordered mesocrystals have been fabricated. Furthermore the dipolar interaction is direction dependent, which renders it improbable to be the guiding force of a 3 dimensional crystal growth. The magnetic interparticle forces get relevant for the self-organization process if a strong magnetic field, for example 0.6 T for 10 nm $\gamma$-Fe$_2$O$_3$ nanoparticles, is applied during the drying. It then dominates the self-assembly [24, 58]. An additional influence on the ordering can originate from entropic effects at higher densities, where a high nanoparticle concentration generates a driving force to order the system to minimize its free energy [24]. In our system it is difficult to decide between the contribution of the van der Waals force and the entropy driven self-assembly (non-interacting), as similar behavior is observed in both systems at the critical density[24], but the selective
Chapter 4 Fabrication and properties of $\gamma$-$\text{Fe}_2\text{O}_3$ nanoparticle assemblies

Evaporating Solvent

(a) Droplet evaporation

Very Dense Solution

(b) Dense solution to reach the critical concentration for nucleation.

Nucleation Area

(c) Nucleation area where the shape and size selective 3D growth can take place.

Mesocystal

(d) Grown mesocystal consists of one kind of particle size and shape. The residual particles are deposited on the ground only with a very short range ordering.

Figure 4.6: Schematic illustration of the model of the self-assembly of an ensemble of mesocrystals. The red box illustrates one nucleation area, which is magnified in the last two pictures.

ordering process described in the next paragraph strongly points to a sizable van der Waals interaction, as it is needed to explain this effect.

The droplet is very thin when reaching the concentration threshold for the self-assembly. This critical value is given, when the droplet reaches the stage of the horizontal drying front (see section 6.3, stage 3), where a circular inward movement of the contact line between the substrate and the end of the droplet is observed. The contact line area fulfills the conditions for the self-assembly and this area is marked with the red box (see figure 4.6b). In this region the mesocystal growth takes place (see section 6.3) and leaves behind the drying front a coffee-stain-like ring of dense material agglomeration [22, 31, 32] at the edge of the substrate and in the inner region well separated mesocrystals. The nucleation starts at the substrate, which could be experimentally shown in section 6.3. Separated particles accumulate on the substrate when reaching a sufficiently small distance to get attracted by the van der Waals force between substrate and particles. It is possible that the attachment of single particles also happens before the threshold is reached, but with a low density only single particles are captured, which can be separated again easily. The particles assemble in a size- and shape selective ordering, as the
growth with the same particles leads to minimization of the surface energy. In other words, differently sized or shaped particles will lead to lattice defects in the crystal structure inside one mesocrystal, which creates a lower packing density and thus an energetically unfavorable state. It is imaginable that a particle, which is much smaller than a regular lattice vacancy can bond only to maximum 3 out of 8 possible neighbors (see Figure 4.7). It thus exhibits less bonding and can more easily be removed from the lattice. A too large particle for the existing vacancy does not fit into the vacancy and is therefore weakly bound as well. Thus the nanoparticles prefer to self-assemble with particles of the same size and shape. In other experiments it has been observed that for a two-dimensional assembly the largest particles order in the center, while the smallest particles accumulate at the periphery [24, 60, 64, 67]. The explanation of Bishop et al, Murthy et al. and Ohara et al. is that the size-dependent magnitude of the van der Waals interactions between the particles lead to a size- and shape selective ordering of the particles [24, 64, 67]. Such an effect has been observed at the ground layers of the investigated systems as well (see Figure 4.9a), where no mesocrystals have grown. Crystal defects or strain occurs when the evaporation was fast and no more suitable particles are available to fill the existing gaps. Dislocations can arise by mechanical pressure on the growing crystal. It is possible only in certain cases, e.g. in binary superlattices, that the nanoparticles order with multiple components inside one superstructure, as the solution has a selected size and concentration ratio and allows an ordering in an energetically favorable high packing density structure [36, 74, 81].

Figure 4.7: Schematics of the size dependent bonding formation in a vacancy of a regular nanoparticle superlattice.

In our case with highly monodisperse nanoparticle solutions, areas with highly ordered 2D nanoparticle assemblies of the same size and shape connected by areas with less ordered particles grow on the substrate. The highly ordered regions are nucleation areas for the 3D mesocrystal growth. The nucleation starts when reaching the critical concentration as described above. Nanoparticles are movable in the solution near to the substrate surface to find an energetically favorable position. It can be imagined that the layers grow similar to the epitaxial growth of thin films. In this situation atoms move on the surface and attach to adatoms, steps or step edges, where they loose their mobility due to the additional bond formation, which in the nanoparticle case is the van der Waals attraction. Ganapathy et al. could show for colloids with diameters of 1.0 or 1.3 μm that colloidal epitaxy obeys the same two-dimensional island nucleation and growth laws that govern atomic epitaxy [45]. Layer-by-layer growth can be assumed in Figure 4.8, where the layers are not closed due to an interrupted mesocrystal growth after drying because of the low concentration used. Differences to the atomic crystal growth are the distribution of size and shape of the particles and the forces involved. The size and shape selective self-assembly leads to a growth of similar particles on the nucleation areas, continuing the growth with the existing structure. Such a shape and size self-segregation could be observed for 3D growth in previous publications [86], as well as in this PhD work for the corresponding system not only in microscopy, but using depth resolved GISAXS (section 4.2.4.4) and single crystal diffraction, as well (section 7.3). The particles start to order in the confined 3D arrange-
Figure 4.8: Illustration of characteristics of the mesocrystal self-assembly: Layer-by-layer growth can be assumed in these SEM pictures, where the layers are not closed because of an interrupted mesocrystal growth after drying due to low solution concentration.

Figure 4.6d. A comparison with the growth modes of atomic films shows remarkable similarities to the island or so called Volmer-Weber growth [19].

The substrate plays an important role for the self-assembly of the ensemble of mesocrystals, as the van der Waals interaction attracts the particles to the surface and thus provides a plane for the crystallization. It defines one crystal axis in the growth direction. The important condition of the coherence between the crystal structure of the substrate and the growing material for thin films for example is negligible in the nanoparticle case, as the particles are much larger than atomic distances and the atomic roughness or mismatch to the lattice has no influence on the binding energy.

The shape and quality of the mesocrystals is governed by various factors. Beside the basic requirements like uniform particles in size, shape and sufficient time for the particles to find a good vacancy in the growing crystals is an important condition to form long range ordered supercrystals (see section 4.2.4.3). The width of the mesocrystals is mainly defined by the region of well ordered nucleation areas. Furthermore the width is always larger than the height of the crystals, which can be explained by the way that the superstructure is growing from the predefined area on the substrate with a given size and a finite diffusion distance combined with a finite number of suitable particles. It is imaginable that a larger time window, a higher solution quality and a higher concentration can produce higher mesocrystals, unless the droplet height needed for the critical concentration is too low. The top of the mesocrystal is mainly flat which is a result of the layer-by-layer growth starting at the substrate plane. Additionally,
4.2 Self-assembly of 3D ordered nanoparticles

(a) Residual nanoparticles mainly sediment on the ground.

(b) Not fully closed base layer.

(c) Cylindrical/hexagonal shape for spheres

(d) Quadratic shape for cubes

Figure 4.9: Illustration of characteristics of the mesocrystal self-assembly measured by SEM: The residual particles are shown on the base layer (figure 4.9a). The size dependent self-assembling is also observed in figure 4.9a, despite the small number of particles. Gaps in the base layer can be seen in figure 4.9b. Figure 4.9c, figure 4.9d illustrate the dependence of the shape of the mesocrystal on the geometry of the unit cell from the nanoparticle superstructure. A more cylindrical/hexagonal shape is grown for spheres and quadratic shape for cubes with small degree of truncation. Figure 4.9d shows also cracks inside the mesocrystal by higher magnification like the crystal consisting of spheres.
it is observed that the planes are almost always closed on the top of mesocrystals. This growth mode can be understood similarly as for thin films, where it is easily possible to move bound atoms on top of a surface and down an edge, as the number of bonds is low, but not up an edge as it costs too much energy. Additionally, it is imaginable that the surface of the droplet (nucleation starts at the substrate-liquid-air interface) can influence the surface as a plane boundary. Dependent on the geometry of the unit cell of the nanoparticle superstructure, the mesocrystals grow in different geometrical bodies like a cylindrical/hexagonal shape for spherical and more quadratic shape for cubic nanoparticles (see figure 4.9c and 4.9d). It can be assumed that mesocrystals form facets along their lattice planes as is found in atomic crystals. In addition it has been observed that some mesocrystals have inclined edges (figure 4.6d and in reality measured by AFM figure 4.10b), while others show straight edges to the substrate (see figure 4.10a and appendix figure A.2). Based on the model of the self-assembly, it is conceivable that a nucleation area which is not completely grown before the 3D ordering starts\(^1\) leads to inclined edges, while the middle part of the mesocrystal is already growing in height, the nucleation area is still growing outwards. The middle part can grow higher than the outer one and so inclined edges.

\(^1\)The first layer of the nucleation area can only grow laterally until it is confined by disordered particles.
4.2 Self-assembly of 3D ordered nanoparticles

4.2.1 Self-assembly procedure

The self-assembly procedure as described in section 4.2.1 for depositing the \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles introduced in section 4.1 yields pillars or islands of nanoparticles on top of a thin ground layer of particles (see figure 4.11). These islands are called mesocrystals and the complete sample is therefore an ensemble of about \( 10^6 \) mesocrystals.

The term mesocrystal is defined as a three dimensional highly ordered assembly of nanoparticles. The particles are arranged like atoms in a crystal and scattering experiments reveal properties of a single crystal (see chapter 7). The size of the building blocks leads to the term “mesocrystal”, which is an abbreviation for “mesoscopically structured crystal” [61]. The

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**Figure 4.11:** Ensemble of mesocrystals measured with AFM for its topography (bottom). The right SEM image shows a view from the top and the left picture shows the nanoparticle order on top of one mesocrystal with higher magnification.

edges are developed. For a terminated nucleation area the particles grow layer-by-layer and the mesocrystal has straight edges. Comparing the results of a self assembly with (medium) and without magnetic field points to the van der Waals interaction as the major driving force for building well ordered mesocrystals, as the ordering pattern is not changed by the magnetic field and the structural coherence length is already very high without it (see section 4.2.4.2). Applying a medium strength magnetic field for different gradient orientation during the process of self-assembly supports the process of building a mesocrystal or works as a source of irritation. The additional influence does not destroy mesocrystal assembly, but shows changes in the mesocrystal’s shape, size and degree of ordering. Only extreme magnetic fields change this result dramatically, distorting or even destroying the resulting mesocrystals (see section 4.2.4.4).

4.2.3 Ensemble of mesocrystals

The self-assembly procedure as described in section 4.2.1 for depositing the \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles introduced in section 4.1 yields pillars or islands of nanoparticles on top of a thin ground layer of particles (see figure 4.11). These islands are called mesocrystals and the complete sample is therefore an ensemble of about \( 10^6 \) mesocrystals.

The term mesocrystal is defined as a three dimensional highly ordered assembly of nanoparticles. The particles are arranged like atoms in a crystal and scattering experiments reveal properties of a single crystal (see chapter 7). The size of the building blocks leads to the term “mesocrystal”, which is an abbreviation for “mesoscopically structured crystal” [61]. The
mesocrystals have a size of 0.5-10 \( \mu \)m in diameter and extend up to 700 nm in height. To give an idea about the number of particles inside one mesocrystal, the sample shown in figure 4.11 with crystals of 2000 nm diameter and 500 nm height incorporate about 5 million nanoparticles in each mesocrystal. The top of the mesocrystal is obviously flat, which is shown in the AFM topography picture (figure 4.11 bottom) and can be estimated from the SEM picture (figure 4.11 top, right). The higher magnification from the top of a mesocrystal shows how nicely the particle are ordered, in this case cubes arranged in a square lattice (figure 4.11 top, left).

The AFM picture (figure 4.11 bottom) illustrates the distribution of mesocrystals on the substrate for a typical sample. The single crystals are arbitrarily orientated in the plane, but with a preferred c-axis orientation defined by the substrate’s surface normal. A sample with arbitrary in-plane rotation of crystals is called a 2D powder. In this case a scattering experiment can access different lattice planes at once as they are realized in different mesocrystals on the same substrate and the pattern shows a lot of reflections without rotating the sample, as would be required for a single crystal. The arrangement of the mesocrystals on the substrate is mostly random without a fixed distance, special order or texture.

4.2.4 Influence of deposition parameters on the mesocrystal characteristics

A knowledge of the influences of different external parameters on the process of self-organization and the final characteristics of the mesocrystals is an important step to optimize the method. An in-situ study of the self-organization can be found in chapter 6. This section provides an overview on how the nanoparticle shape, the magnetic field strength, gradient direction and the evaporation time can affect the mesocrystals in their end characteristics like space group, shape, size, surface coverage or degree of order.

4.2.4.1 Nanoparticle shape

A variation of the shape of the nanoparticles for a drying-induced self-assembly process leads to different crystal structures. The spherical particles arrange themselves in a rhombohedral lattice, while the cubic nanoparticles with high degree of truncation self-assemble in a tetragonal structure [33, 35]. This effect can be seen globally in the GISAXS pattern (3D) and locally in microscopy pictures (2D) of the respective systems figure 4.12 and figure 4.13. In both cases the scattering pattern shows sharp reflections, which is an indication for a good crystalline order.

The analysis of the space group is done according to well established crystallographic methods [7, 11]. In the special case of highly ordered mesocrystals, all reflections (hkl) from different directions arise in one single GISAXS pattern without rotation of the sample. The flat Ewald sphere in small angle scattering, as well as the 2D powder property with the in-plane orientation average allow this simultaneous observation. The Bragg peaks resulting from scattering of the reflected beam are weak under the angle of incidence used here and are not indexed. These arise from a scattering process with a reflection at the substrate and are thus dependent on the angle of incidence. The intensity of these Bragg peaks is much lower than the one of Bragg
4.2 Self-assembly of 3D ordered nanoparticles

![GISAXS pattern (SWING/Soleil)](image)

![SEM (top) and TEM (bottom)](image)

Figure 4.12: Structural analysis of an ensemble of mesocrystals formed with long waiting time from spherical building blocks of radius 5.01 nm self-assembled under a magnetic field of 80 mT and gradient up ($D_{Lg}^{1.68\times80}$). The measurement was done under an angle of 0.4° and with a wavelength of 1.77 Å. Reflections of the GISAXS pattern are indexed according to the rhombohedral structure discussed in the text. The Bragg peaks resulting from scattering of the reflected beams are weak under this angle and not indexed. The SEM picture is made from the top of a mesocrystal, the TEM picture shows a vertical cut through a mesocrystal and therefore a plane perpendicular to the substrate.

peaks from direct scattering as the reflection at substrate strongly reduces the beam intensity, especially at larger angles of incidence.

The spherical nanoparticles self assembled in an ensemble of mesocrystals, in which the average lattice constant of single mesocrystals are $c = 31.3 \pm 0.1 \text{nm}$ for the crystal direction perpendicular to the substrate and $a = 12.7 \pm 0.1 \text{nm}$ in-plane. These parameters are extracted from all well visible reflection positions in figure 4.12a. Indexing of the GISAXS reflections yields an extinction rule of $-h+k+l = 3n$, which is consistent with a rhombohedral space group $R\overline{3}m$ (No. 166), a distorted form of a closed packed structure with face centered cubic (ABCABC) stacking. The unit cell of the rhombohedral lattice is shown in figure 4.14. Due to the 2D powder characteristics, the indices $h$ and $k$ cannot be distinguished, so the reflections could be indexed with the reverse lattice with the corresponding extinction rules $h-k+l = 3n$, too. The alternative possibility for the expected closed packed spheres with an hexagonal lateral symmetry is a hcp (ABAB) stacking type, which corresponds to the space group $P 6_3/mmc$ (No. 194). This case can be excluded, because the extinction rule of $l = 2n$ could not be observed. The present fcc stacking confirms the preference of the face centered cubic structure over a hexagonally closed packed crystal. [26, 50, 95]. Heitkam et al. showed with model experiments that a mechanical instability in the self-assembly of the fourth layer for the hcp stacking leads to a rearrangement of the hcp into fcc packing [50]. Bolhuis and Frenkel showed
that the free energy of the fcc stacking is smaller than for the hcp one, following a theoretically more stable fcc stacking [26]. The microscopy pictures confirm the results of the structural GISAXS analysis. Hexagonal layers are observed on top of the mesocrystals by SEM (figure 4.12b top) and the TEM picture with a vertical cut through a mesocrystal shows the (ABCABC) stacking (figure 4.12b bottom). The lattice constant determined as $a = 12.7 \pm 0.1$ nm corresponds to a face centered cubic array of spherical nanoparticles with a diameter of 10.02 nm and 1.34 nm shell thickness. The shell thickness lies in the range of the shell thicknesses measured by SANS between 1.1 and 1.6 nm [33, 103]. The extracted value for the $c$ lattice constant with $c = 31.3 \pm 0.1$ nm is slightly higher than the one expected for a perfect fcc stacking of 31.1 nm for this type of structure. The expansion of only 0.6% in the [001] direction of the rhomboedral cell shows a nearly perfect fcc structure.

The cubes self-assemble in an ensemble of mesocrystals, where the average lattice constant of single mesocrystals are $c = 23.9 \pm 0.1$ nm and $a = 14.2 \pm 0.1$ nm. Indexing of the GISAXS reflections in figure 4.13a yields an extinction rule of $h + k + l = 2n$, which is consistent with a $I4/mmm$ (No. 139) space group with a body centered tetragonal (bct) unit cell. The unit cell of the bct lattice is shown in figure 4.14. For the cubic particles, the local microscopy images confirm the results of the structural GISAXS analysis too, which give the average over the sample. The square symmetry is observed on top of the mesocrystals by SEM (figure 4.13b top) and the TEM picture with a vertical cut through a mesocrystal shows the tetragonal
4.2 Self-assembly of 3D ordered nanoparticles

Figure 4.14: Schematic unit cell of the rhombohedral structure of the nanospheres (left) and the body centered tetragonal (right) structure of nanocubes mesocrystal.

lattice (figure 4.12b bottom). The simple cubic symmetry can be excluded from TEM and the selection rules, which clearly show a bct lattice. The crystal structure observed originates from the anisotropic shape of the nanoparticle.

In general, anisotropic particles favor a face-to-face packing to maximize the van der Walls interaction energy [86]. In this case, the (100) facets of the nanocubes touch each other in one layer. The preference of bct against simple cubic in the 3 dimensional direction can be explained by the truncated shape of the cubes. Each square layer offers a gap between neighboring particles in the plane, within which the particles of the next layer can arrange themselves. The gaps are generated by the high degree of truncation of the cubes. A higher degree of truncation favors the bct structure until the particles get too spherical, favoring the fcc structure. A lower degree of truncation would favor a simple cubic arrangement [33]. In detail, the energy of attractive van der Waals interactions for face to face stacking is inversely proportional to the square of the distance between two faces (\( \sim \frac{1}{r^2} \)), while for the edge-to-edge stacking the interaction energy is inversely proportional to the separation distance (\( \sim \frac{1}{r} \)) [86]. The statement of Song et al. leads to the consequence that the van der Waals interaction is stronger for the face to face configuration than for edge to edge or corner-to-corner configuration for short distances between the particles. Consequently, the perfect cubes prefer the face-to-face stacking, arranging in simple cubic stacking as in this configuration all surfaces have the smallest distance between each other and the maximum van der Waals energy is reached. For the truncated particles a new surface is formed at the corners of the cubes and yields additional coupling areas. Increasing the degree of truncation within simple cubic stacking leads to corners with much more distance to each other.

<table>
<thead>
<tr>
<th>sample ID</th>
<th>selection rule</th>
<th>space group</th>
<th>a [nm]</th>
<th>c [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{S, 5.01}^{Lg1.68, 80} )</td>
<td>( h + k + l = 3n )</td>
<td>R3m</td>
<td>12.7 ±0.1</td>
<td>31.3 ±0.1</td>
</tr>
<tr>
<td>( D_{C, 10.9, 0.8}^{XLg1.68X} )</td>
<td>( h + k + l = 2n )</td>
<td>I4/mmm</td>
<td>14.2 ±0.1</td>
<td>23.9 ±0.1</td>
</tr>
</tbody>
</table>

Table 4.3: Results of the structural analysis of the ensemble of mesocrystals formed with long/extra long waiting time from spherical/cubic building blocks of radius 5.01 nm/edge length 10.9 nm and degree of truncation of 0.8 self-assembled under an magnetic field of 80 mT and gradient up/without a magnetic field (\( D_{S, 5.01}^{Lg1.68, 80} / D_{C, 10.9, 0.8}^{XLg1.68X} \)). These outcomes are an average over the ensemble of mesocrystals.
while the distance of the faces stays constant. The simple cubic case gets less and less favorable as the interaction energy between the corners get much smaller. A transition to the bct structure is given when the interaction energy is too low compared to the face-to-face arrangement, so that the particles start to order in bct structure \[33\]. Whereas the distance between the faces gets a little bit bigger, the corners get much closer, so that the competing interactions are in balance. An extreme increase of the degree of truncation leads to order the particles in an hexagonal lattice, which is shown in the high resolution TEM images in figure 4.3c. These examples give an impression of the importance of the relation between cubic ordering and degree of truncation.

### 4.2.4.2 Magnetic field

To optimize the self-assembly, a systematic variation of the magnetic field influence has been studied which is presented in this section. For this purpose a variety of magnetic field and field gradient strengths (80 mT magnet with 18 mT/cm, 2 mT with 0.3 mT/cm, homogeneous field of 4 mT and no field) and different directions of the gradient were applied during the self-organization of the nanoparticles. The gradient direction is always aligned with the field direction. Gradient directions away from the sample surface \(\perp\) (gradient up), towards the sample surface \(\parallel\) (gradient down) and along the substrate’s surface \(\perp\) (gradient in-plane) have been investigated. The other drop casting parameters were kept fixed. The characterization was performed locally by SEM and AFM on different positions and in average over a large sample area by GISAXS measured at SWING, Soleil. The GISAXS patterns were analyzed by fitting selected peaks with the fitting routine described in section 5.3.2. The modeling of scattering patterns of an ensemble of mesocrystals will be explicitly discussed in chapter 5. The systematic investigation of the field dependence is demonstrated here with spherical particles of the solutions \(S^8\) and \(S^4\), respectively. The GISAXS results for different external field parameters are presented in figure 4.15 and figure 4.16. The quantitative parameters extracted for these samples are listed in table 4.4 and figures 4.17 - 4.23. Additional experimental images can be found in the appendix section A.1.

A good overview over the influences of various parameters for the \(S^8\) solution can be obtained from the GISAXS patterns (figure 4.15). The seven pictures show the GISAXS patterns from the mesocrystal assemblies deposited at different field configurations: The symbol at the upper right corner indicates either the direction of the field gradient (\(\perp, \parallel\), \(\perp\)) or zero field conditions (\(X\)). The colour of the symbol represents the strength of the field: \(\perp\) means a low field configuration with gradient up, while \(\perp\) is the analogon for a strong magnetic field. These field configuration symbols are also part of the sample ID, e.g. \(D_{Lg1}^{6.8<\perp}\) describes a sample deposited in a low field (2 mT) perpendicular to the substrate with gradient up.

The pictures in the left column show the GISAXS patterns of all mesocrystal assemblies prepared at small magnetic fields. The pictures to the right compare with their neighbour on the left by a different field strength and the same orientation of field and field gradient. The application of different field settings during the self-assembly (figure 4.15) shows influences on some characteristics of the sample while others stay unaffected. The gradient up fields (\(\perp, \parallel\)) support the self-assembly, the gradient down configurations (\(\parallel, \perp\)) have a negative impact on the mesocrystal growth. The peaks are found broader in the \(\parallel\) pictures compared to the \(\perp\) pictures at the same field strength. Furthermore the self-assembly in higher fields (\(\perp, \parallel\)) shows a better superstructure quality than the low field configurations (\(\perp, \parallel\)). The low homogeneous field
4.2 Self-assembly of 3D ordered nanoparticles

**Figure 4.15:** Ensembles of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml ($S_S^{8.4}$) at different field conditions (low field: gray; strong field: black, Δ: gradient up, ⊶: gradient in-plane, ⋂: gradient down, X: without field, ↑↑: homogenous field perpendicular to the sample surface). The measurements were performed at an angle of incidence of $0.4^\circ$ and with a wavelength of 1.77 Å at SWING, Soleil.
Figure 4.16: Ensembles of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $4.7 \times 10^{14}$ NP/ml ($S_S^{8.4}$) at different field conditions (low field: gray; strong field: black, $\Delta$: gradient up, $\triangleright$: gradient in-plane, $\triangleright\triangleright$: gradient down, $\times$: without field, $\uparrow\uparrow$: homogenous field perpendicular to the sample surface). The measurements were performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.
4.2 Self-assembly of 3D ordered nanoparticles

and the zero field setup ($X$) show an intermediate quality between the low and high fields. These results have been reproduced for samples grown from a solution with lower concentration of the same nanoparticles $S_{S}^{4.7}$ (figure 4.16).

It is remarkable that the magnetic field configurations have no influence on the resulting mesocrystal structure. All samples show the known $R_{3}m$ space group for the assemblies with spheres with minimal lattice constant variations of a few %. The major influence on the crystal structure of the mesocrystals is given by the morphology of the nanoparticles, which produces a close packed structure to minimize the energy for spherical particles (see section 4.2.4.1).

The quality of the ordering shows differences between high field/gradient and the low field/gradient configurations. The first two (figure 4.17, figure 4.18) yield long range ordered assemblies, at which the quality of the $D_{S}^{Lg1.68,80}$ sample is slightly better, mainly expressed as larger and higher mesocrystals. The homogeneous field (figure 4.21) as well as the zero filed setup (figure 4.22) produced well ordered superstructures nearly as good as with the strong field configuration. The correlation lengths are comparable to the locally measured sizes from the microscopy. The good order with low surface defects is verified by SEM pictures on top of a mesocrystal. The $H_{X}$ configuration showed, in average, the largest mesocrystals with a correlation length of around 1200 nm in-plane and 430 nm in the height. The tilting of the mesocrystals is negligibly small, while a random variation of the lattice constant of 0.1% is observed only for the zero field configuration. This can be noticed in the scattering picture features as a modified peak shape getting broader with higher Q values. In the case of this sample the distribution seems to be non-isotropic, e.g. with different lattice constant distributions for the in-plane and out-of-plane directions. As the underlying directional distribution is not known, the measurement contains a 2D powder average and many additional parameters with similar impact on the peak shapes would be needed, a fit of this anisotropic broadening could not be performed. The $D_{S}^{Lg1.68,80}$ configuration (figure 4.18) exhibits further structural features in addition to the main structure. Preferred directions of the mesocrystal/crystallites tilting are present indicated by sharp peaks lying on the Debye-Scherrer-rings. For example the (104) and (006) are both found duplicated rotated 22° with respect to their main peak. Apparently, these crystallites have a c-axis rotated by this value using from the substrate surface normal.

In contrast, the samples with low gradient configuration (figure 4.19, figure 4.20, figure 4.23) have many visible surface defects and imperfections which can be observed in SEM and which are slightly reflected in the lower in-plane correlation length averaged over the ensemble. Additionally, the mesocrystal surfaces are bent, which is also confirmed by the GISAXS fit in the tilting angle of 2° for the sample $D_{S}^{Lg1.68,2}$. All three samples show Debye-Scherrer rings, where the in-plane gradient sample produces weaker and broader ones demonstrating a not so high number of 3D disordered objects with smaller sizes than the mesocrystals. Based on the sharpness of the rings for gradient down it is assumed that this scattering pattern is produced by small mesocrystals or crystallites, which are arbitrarily rotated against each other. For the $D_{S}^{Lg1.68,2}$ and $D_{S}^{Lg1.68,2}$ sample a superposition of extreme broad peaks with very sharp peaks can be observed. This indicates that besides a broad distribution of lattice constants for most of the ensemble, there exists a fraction of mesocrystals with a well defined lattice constant. These peaks are extremely sharp which indicates the high quality of some mesocrystals.

The Yoneda lines observed for the $D_{S}^{Lg1.68,80}$ samples are weak and narrow, while other samples like $D_{S}^{Lg1.68,2}$ have a more intense and broader Yoneda line. The position of the
Figure 4.17: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \cdot 10^{14}$ NP/ml in a magnetic field of 80 mT and gradient up ($D_{5.01}^{g1.68 \& 80}$). The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

Figure 4.18: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \cdot 10^{14}$ NP/ml in a magnetic field of 80 mT and gradient down ($D_{5.01}^{g1.68 \& 80}$). The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil. Peaks originating from a rotation of the main structure and their original positions are marked.
4.2 Self-assembly of 3D ordered nanoparticles

Figure 4.19: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 2 mT and gradient up ($D_{S,5.01}^{g1,68,2}$). The GISAXS measurement was performed at an angle of incidence of 0.4 ° and with a wavelength of 1.77 Å at SWING, Soleil.

Figure 4.20: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 2 mT and gradient down ($D_{S,5.01}^{g1,68,2}$). The GISAXS measurement was performed at an angle of incidence of 0.4 ° and with a wavelength of 1.77 Å at SWING, Soleil.
Chapter 4 Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

Figure 4.21: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \cdot 10^{14}$ NP/ml in a homogeneous magnetic field of 4 mT perpendicular to the sample surface ($D_{s,5.01}^{Lg1.68}S_8$). The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

Figure 4.22: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \cdot 10^{14}$ NP/ml ($S_8^{D_{g1.68}}$) without applied magnetic field ($D_{s,5.01}^{Lg1.68}X_8$). The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.
4.2 Self-assembly of 3D ordered nanoparticles

Figure 4.23: Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 2 mT and gradient in-plane ($D_{Lg1.68X}^{\perp} > 2S, 5.01$). The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

Yoneda line depends on the critical angle $\alpha_c$ and its intensity on the substrate-layer-air contrast, which both depend on the laterally averaged scattering length density (SLD) (section 2.2.5). The shape and intensity of the Yoneda line depends on the relation of the coherence length of the experiment to the size and shape of the mesocrystals. For example, a sharp line can be observed for a coherence length smaller than the mesocrystal size when perpendicular edges are present. A broad Yoneda line can be induced by smaller coherence length than mesocrystal size with inclined edges or by a long coherence length compared to the mesocrystal and many mesocrystals of different heights. Generally speaking, the higher the uniformity of the SLD inside the coherence volume, the sharper the Yoneda line. The SEM observations show huge mesocrystals with straight edges for $D_{Lg1.68X}^{\perp}$ with sizes between 1 and 4 µm and for $D_{S, 5.01}^{Lg1.68\perp}$ between 3 and 7 µm, which have big distances between the crystals, while the other samples show smaller mesocrystals with inclined edges separated with a lower distance and sizes of around 0.2-2 µm. From this complementary investigation it can be concluded that the narrow Yoneda lines in the GISAXS patterns arise from the scattering of individual mesocrystals, as the correlation length ($\leq 10$ µm) is too small to scatter coherently between mesocrystals at these large distances. The perpendicular edges lead to no SLD distribution inside the coherence length and thus to no different critical angles. The other sample $D_{S, 5.01}^{Lg1.68\perp}$ has height differences measured by AFM (see appendix) so that it can be assumed that in this case the SLD profile induced by the inclined edges inside the coherence volume is the important factor which induces a depth dependent $\alpha_c$ distribution and thus the broader Yoneda line, while for $D_{S, 5.01}^{Lg1.68\perp}$ the height distribution of different mesocrystals inside the coherence volume can be the major cause.

Further features could be observed by microscopy investigations. The SEM showed that the zero field/homogeneous and gradient up field configurations produce cylindrical mesocrystals with a
Table 4.4: Results from the systematic investigation of the field influence on the outcome of the mesocrystals growth. Microscopy as well as depth resolved GISAXS experiments reveal different characteristics and the combination leads to a good description of the quality of the sample. The parameters ε\(\times\)y/z are the average mesocrystal in-plane/out-of-plane correlation length and \(\sigma\)rad/\(\sigma\)tilt the radial/tangential standard deviations describing a random variation of the mesocrystal lattice parameters and tilting of the c-axis away from the substrate surface. The above text explains the fundamental assumptions on the random distribution of the mesocrystal lattice parameters and the c-axis orientation, which are the basis for the interpretation of the experimental data. The experimentally found development describes a typical mesocrystal with a small number of surface defects and a strong correlation of the in-plane parameters. The parameters ε\(\times\)y/z are the average mesocrystal in-plane/out-of-plane correlation length and \(\sigma\)rad/\(\sigma\)tilt the radial/tangential standard deviations describing a random variation of the mesocrystal lattice parameters and tilting of the c-axis away from the substrate surface. The above text explains the fundamental assumptions on the random distribution of the mesocrystal lattice parameters and the c-axis orientation, which are the basis for the interpretation of the experimental data. The experimentally found development describes a typical mesocrystal with a small number of surface defects and a strong correlation of the in-plane parameters.

Due to the multiple peak structure, these parameters could not be determined from the fitting routine.
4.2 Self-assembly of 3D ordered nanoparticles

Flat surface, which cover around 23% (determined by AFM) of the substrate area. Additionally, small mesocrystals between the large ones are observed with a height of 100 nm and 100-800 nm in diameter only for $D_{S, 5.01}^{Lg1.68, S80}$. The $D_{S, 5.01}^{Lg1.68, S80}$ and the low field self-assembled mesocrystals have a less defined shape with tilted surfaces and inclined edges and cover 35% of the surface. These mesocrystals are much smaller.

In summary the applied magnetic field and field gradient influences the ensemble of mesocrystals grown in shape, size and quality of ordering. The conclusion that the self-assembly in an applied field can improve the long range order of the resulting structure [14, 24, 33, 84] is supported here, but in more detail it turns out to be strongly dependent on the direction and strength of the field and the field gradient. A field applied in the growth direction supports the self-assembly and improves the quality of the ensemble of mesocrystals, while the obverse hinders the mesocrystal growth and worsen the result. Furthermore, a stronger gradient lets grow more cylindrical, flat and higher mesocrystals compared to lower gradients. The gradient is in this case the important factor, as a homogeneous low field produces nearly comparable good mesocrystals as a field applied in the growth direction. The self-assembly process itself is not dominated by the magnetic interaction as the configuration with and without field result in the same structural characteristics.

The application of the field and the field gradient in the growth direction has a positive effect on the growing mechanism. The force in the growing direction can assist the 3D growth pulling the nanoparticles up, compensating the gravity force, acting in the opposite direction. It is a lot easier for the particles to detach from the surface and move around to find an energetically favorable site. This higher mobility can produce larger nucleation centers to achieve larger crystals as well as the possibility to grow higher. Cylindrical mesocrystals with a flat surfaces and sharp edges can be produced with a layer-by-layer growth, which is favoured if the nucleation area is nearly fully grown before the 3D ordering starts.

The samples produced with a field gradient opposite/perpendicular to the growth direction have an additional force which disturbs the process of self-assembly. In addition to the gravity it pulls the particles towards the substrate, so that the mobility of the particles is reduced. The dipole-dipole attraction introduces another disturbance in the in-plane field case, as it acts in a direction perpendicular to the growth. The shape and size selective self-assembly develops smaller nucleation areas due to insufficient time and the lower ability of the particles to move on the surface. It is also imaginable that the volume growth is preferred over the layer-by-layer growth. The additional force to the substrate can favor a 3D growth before the nucleation area is fully developed, which can explain the inclined edges. The missing mobility can cause many imperfections on the surface like lattice vacancies, tilted mesocrystals in preferred directions and the 3D powder characteristic.

4.2.4.3 Evaporation time

The evaporation time of the solution droplet is an additional factor of great importance for the process of self-assembly. It can influence the size, shape and quality of the resulting mesocrystals. First characterizations were performed by SEM and GISAXS measured at ID01, ESRF or in Risø. The samples measured at ESRF were self-assembled during an in-situ GISAXS experiment. In this case a time dependant recording was possible (section 6.1 and section 6.2). The investigation of the time dependence is demonstrated with cubes of the solution $S_{C84}$. and
Figure 4.24: Ensemble of mesocrystals built up by cubic building blocks of edge length 10.9 nm and degree of truncation of 0.8 self-assembled within 12 min ($D_{C,10.9,0.8}^{3h1.08\times36}$). The measurement was performed at an angle of 0.3° and with a wavelength of 1.27 Å.

Figure 4.25: Ensemble of mesocrystals built up by cubic building blocks of edge length 10.9 nm and degree of truncation of 0.8 self-assembled within 250 min ($D_{C,10.9,0.8}^{1g1.68\times36}$). The measurement was performed at an angle of 0.3° and with a wavelength of 1.27 Å. Some reflexes of the second structure are marked with black points.
4.2 Self-assembly of 3D ordered nanoparticles

Figure 4.26: Ensemble of mesocrystals built up by spherical building blocks self-assembled with shorter and longer evaporation time for a gradient down configuration. The measurement was performed at an angle of 0.4° and with a wavelength of 1.54 Å.

spherical particles of the solution $S^8_{8}$. Parameters other than the evaporation time were fixed as well as possible.

The sample self-assembled with a short evaporation time of 12 min produces a GISAXS pattern with relatively broad and low intensity peaks, which have a fast decay in intensity to higher Q's (figure 4.24a). This indicates a system with a low coherence of the scattering planes, either because the correlations decay with distance or because a low number of scattering planes exists. The fast decay to higher Q values can be caused by a lattice constant (peak broadening for higher Q) and the local disorder (Debye-Waller factor) caused by e.g. nanoparticle size distribution. For an interpretation of the low coherence of the scattering planes the SEM pictures are consulted (figure 4.24b). One finds small mesocrystals with an average size of 200 nm and a low height showing a high surface coverage with less gaps between the crystals. The small mesocrystals can be the reason for the low coherence. This statement is backed up by the fact that the structure on top of every single mesocrystal looks coherent. Additional crystal defects for example in the bulk cannot be ruled out as additional contribution. The SEM shows also that the mesocrystals have no well defined shape.

Extending the evaporation time leads to sharper and stronger peaks persisting up to higher order (figure 4.25a). These features of the scattering pattern suggest a higher correlation length in contrast to the sample produced with short evaporation time. The SEM pictures (figure 4.25b) confirm these, showing large mesocrystals up to 2 µm in edge length and a larger height. The crystals grown are more separated and have a cubic shape.
Both cases with cubic nanoparticles indicate a weak second structure in the scattering pattern, which has not been determined in the analysis. For the quickly evaporated sample it is smeared out, while the other sample shows small sharp reflexes (see figure 4.25). The extended time expectedly affects the second structure as well. A fitting of the datasets as done in section 4.2.4.2 was not possible, due to the unknown structure and the overlap of reflections from both structures.

The effect of extending the evaporation time for other field configurations which - as shown above - produces less well ordered mesocrystals is shown in figure 4.26. For these sample preparations the in-situ setup was not available to define an exact time measurement, so the description here is just shorter and longer time. It is obvious that the residual Debye-Scherrer ring, crossing the point -0.05 Å, 0.06 Å, vanishes with longer evaporation time. A higher peak intensity is observed, too. A second example with an in-plane field configuration is shown in appendix figure A.11 and confirms the present observation.

It has to be emphasized that sufficient time for each particle to find a good place in the growing crystals is essential to form long range ordered supercrystals. More time can lead to growth of larger nucleation areas, as the time allows a diffusion of fitting particles to the growing areas and larger nucleation areas enable a growth of wider mesocrystals. Furthermore increasing the time allows the possibility to grow higher mesocrystals for the same reasons. In addition, the increased evaporation time can reduce the number of defects and thus increase the correlation length. Obviously, the improvement of the structural quality is limited as the diffusion radius of the particles scales with the square root of time (section 2.1.1) and an extension of the timescale has experimental limitations. Furthermore the growth of the nucleation areas will be limited, when a closed layer has been formed. The appearance of the different surface coverage can be explained by the short time of the high concentrated nucleation stage where mesocrystals are growing on every small nucleation area, while a longer nucleation stage allows development of well separated and ordered nucleation areas where the particles have time to find an energetic optimal position. Whether a longer time is only necessary in the nucleation stage or already before this stage in the dense solution as well, cannot be answered from these investigations and chapter 6 will go more into detail about the stages.

4.2.4.4 Extraordinary Conditions

This section deals with the influence of self-assembly parameters behind the typical magnitude. New conditions can lead to complete changes of the outcome of the self-assembly. As has been done for the moderate parameter variations, the outcome of these different extraordinary parameters will be described in separate paragraphs split by the different extraordinary parameters.

Nanoparticle shape

The influence of a shape distribution dependent self-assembling can be investigated with a multicomponent nanoparticle solution, drying under typical conditions. A shape selective self-segregation for spherical, as well as for anisotropic nanoparticles was observed by microscopy investigations and explained by the size-dependent magnitude of the van der Waals interactions between the particles [24, 60, 64, 67, 86]. In this work the shape dependent self-assembly between spherical (S_8^S: r=5.01 nm, 8.4·10^{14} NP/ml) and cubic particles (S_8^C: a=10.9 nm, Trunc =0.8, 8.4·10^{14} NP/ml) in 3 dimensional systems is investigated. Both components have been
4.2 Self-assembly of 3D ordered nanoparticles

(a) GISAXS - Indicated by white triangles is the bct and by black circles the rhombohedral structure (lab source/Risø). The measurement was performed at an angle of $0.4^\circ$ and with a wavelength of 1.54 Å. The line at $Q_z = 0.06$ Å$^{-1}$ is a detector saturation effect.

(b) SEM - The lighter areas are the results of a charging effect from higher resolutions scans, done before, see figure 4.28a and figure 4.28b.

**Figure 4.27:** Ensemble of mesocrystals self-assembled from spherical and cubic building blocks at once self-separated into mesocrystals. The result of the shape induced self-segregation is shown in the SEM pictures with obvious structural diversity on top of different mesocrystals (the overview at lower magnification is shown here), as well as in the existence of sharp mesocrystals GISAXS peaks of two different space groups.
Chapter 4 Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

Figure 4.28: Ensemble of mesocrystals self-assembled from spherical and cubic building blocks at once self-separated into mesocrystals. The result of the shape induced self-segregation is shown in the SEM pictures with obvious structural diversity on top of different mesocrystals. The darker areas are the results of a charging effect from previous higher resolutions scans.
4.2 Self-assembly of 3D ordered nanoparticles

Figure 4.29: Light microscopy images of an ensemble of mesocrystals self-assembled under an in-plane magnetic field of 30 mT and gradient of 70 mT/cm. The arrow shows the direction of the field lines.

mixed deliberately together in one solution and studied with microscopy and GISAXS. This is the first in depth observation of well separated 3D ordered structures within one sample.

The sample prepared with the multicomponent solution shows two separated well grown mesocrystal types in the SEM image figure 4.27b, which shows, from the top, different structures in higher magnification. One mesocrystal has a hexagonal layer on top figure 4.28a, while the other shows a quadratic structure figure 4.28b. To get the 3D structures and a hint about the overall structural distribution in the sample, the GISAXS pattern has to be analyzed. The diffractogram exhibits sharp mesocrystal peaks of two different 3D structures. This means that highly ordered mesocrystals are grown in one sample differing in their nanoparticle superstructure. The major part of the intensity, and therefore larger number of mesocrystals, comes from the known rhombohedral structure R̃3m (black) with a=12.11 nm and c=29.22 nm, the rest has the tetragonal structure I4/mmm (white) with a=12.32 nm and c=16.76 nm found in deposited cubes. The small c-axis lattice parameter is the result of the small cube size of 8.9 nm and a truncation of 0.88 [35], of the solution which was used in this case. The high truncation can lead to a compression in the direction of the c-axis, which expands the a-axis. The observed extra peaks at Qx = 0.063 Å⁻¹ and Qy = 0.016 Å⁻¹ and its mirror position can be an indication of a similar superstructure as was observed by Disch et al. for the same particles [35] and the SEM picture shows a similar superstructure on the surface. A precise superstructure determination is not possible due to the low intensity of the lab source.

This experiment shows that the shape dependent self-segregation holds not only for different sizes, but for shape mixtures as well, and supports the statements in the model of the mesocrystals growth from section 4.2.2. The size and shape selective van-der-Waals force as well as shape selective vacancies lead to a selective ordering of the different particles. Mesocrystals form from similar kinds of particles, each highly ordered, while the ensemble contains diverse mesocrystals of different kinds of building blocks and structures. This is the first observation of two well separated 3D structures within one sample.

Magnetic field
Applying a very strong magnetic field with a gradient during the self-assembly of γ-Fe₂O₃
nanoparticles leads to a completely different crystallization behaviour as the one reported in section 4.2.4.2 for smaller fields. A field of 30 mT and gradient of 70 mT/cm applied parallel to the substrate induces elongated mesocrystals oriented along the H-field lines (see figure 4.29). The average mesocrystal size is in the order of 20 µm in width and ≈ hundred µm in length. The large gradient of the external magnetic field is the most likely cause of this growth pattern.

The asymmetric mesocrystal shape can be explained by the interplay of the van der Waals and the directional field induced dipole-dipole interaction between the magnetic nanoparticles enhanced in this special case to allow the formation of chain like structures. The additional directional force changes not only the shape of the mesocrystals, but allows the growth of much larger mesocrystals. Further details of this sample for example, the mesocrystal structure, have yet to be determined.

In another extreme magnetic field configuration with out-of-plane gradients during the drying of the droplet, a huge 3D nanoparticle assembly, visible to the naked eye, has been produced (see figure 4.30a made with a camera). The formation has a size in the mm-range, therefore referred to as macro-polycrystal, and is the first observed nanoparticle assembly in this dimension. The assembly looks like a droplet of a ferrofluid in a strong magnetic field as e.g. shown by Timonen et al. [91]. The macro-polycrystal as well as the ring around it has a metallic glossiness and a bluish black color as expected from maghemite material.

For a more detailed surface investigation normal SEM microscopy was consulted. The lowest possible magnification is shown in figure 4.30b and the huge object is barely visible. In this configuration the details of the pillar structure are not visible, but the mesoscopic surface structure inside the ring can be resolved. Densely arranged mesocrystals are visible at the edge of the ring. The size of the structures increases with decreasing radius and looks more like filaments with an inner structure. At the border of the macro-polycrystal filaments of nanoparticle assemblies appear as if pulled up to the pillar. In figure 4.31a a higher magnification is chosen and it is visible that the whole pillar consists of further branched formations, a dendrite like structure, already observed in other nanoparticle systems [37, 88].
4.2 Self-assembly of 3D ordered nanoparticles

GISAXS measurements were performed at the lab source in Risø. Figure 4.32a shows the scattering pattern of the macro-polycrystal. The beam is scattered from the middle of the pillar without hitting the substrate in a typical SAXS geometry. Rings are visible as indication of a 3D powder. The sharpness of these rings proves a relatively large correlation length and thus an existing order in the system. To define the average correlation length a Voigt function is fitted to the peaks from the radially integrated intensities. A value of 550 nm for the average correlation length is received, which indicates an existing long range order inside the macro-polycrystal consisting of many well ordered mesocrystals rotated against each other. This order belongs to the R3m structure, known from the corresponding mesocrystals. Furthermore a texture can be observed on the Debye-Scherrer-rings, which indicates an inhomogeneously distributed 3D powder of mesocrystals. A measurement on the ground next to the macro-polycrystal (figure 4.32b) shows a mixture of 3D powder and partly oriented mesocrystals. Sharp peaks in Q_y direction indicate a well ordered in-plane structure and the broad peak in Q_z direction suggests the presence of a thin film of nanoparticles.

The sharp peaks on the rings can be explained by a few mesocrystals with larger correlation length. Additionally, the pillar height is much larger than the maximal measured droplet height in the in-situ experiments (< 500 μm), which makes it even more fascinating, as no obvious differences were observed during the drop casting. Similar to the previous in-plane gradient study, the mesocrystal growth follows the field lines, moving to the sample center and even piling up above the liquid surface. The strong directional force of the field and field gradient align the magnetic moments of the nanoparticles and let them order as long mesocrystals chains mainly through the dipole-dipole interaction. The single chains are packed closely to each other, whereas the lower crystal can be assumed as a new basis for a new chain formation and the macro-polycrystal growth. If this formation happens in a fluid layer or outside the droplet can not be clarified until now. Furthermore with this experiment it is shown that a substrate is not necessary for the formation of good mesocrystals inside a dipole-dipole formation dominated system, although these are rotated against each other while a growth on a substrate leads to a preferred orientation of one crystal axis.
Chapter 4 Fabrication and properties of $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies

Figure 4.32: GISAXS/SAXS measurements of a macro-polycrystal self-assembled with $\gamma$-Fe$_2$O$_3$ nanoparticles at the lab source in Risø. The measurement was done in transmission geometry (a) and under an angle of 0.4° (b) with a wavelength of 1.54 Å.
4.2 Self-assembly of 3D ordered nanoparticles

![TEM - spheres](a) ![TEM - cubes](b)

![SEAD - spheres](c) ![SEAD - cubes](d)

**Figure 4.33**: SEAD pattern of one mesocrystal with its corresponding real space TEM image for spherical and for cubic building blocks. The SEAD images are taken from around a 10x10 nanoparticle cluster from the mesocrystal mapped. The white arrow with the letter n defines the growth direction of the mesocrystal.

4.2.5 Crystalline orientation of the nanoparticles

So far I have considered the individual nanoparticles as the elementary building blocks forming the mesocrystals when they arrange in a periodic manner. Now I go one step further and consider in addition the atomic structure of these nanoparticle building blocks. We can ask the question, how the atomic lattice planes of different nanoparticles are oriented with respect to each other. Can we achieve an orientational alignment of the atomic lattice planes within the entire mesocystal? How can we achieve such an order and to which degree? What is the effect on the magnetic properties of the mesocystal? As has been reported in [41, 73], single domain magnetic nanoparticles inside a solvent can align their easy axis in the magnetic field direction and allow a partial orientation by the application of an external field during the deposition process. It is expected that this formation stays stable in this preferred orientation after deposition. The question arises how this effect can be observed in an ensemble of mesocrystals of such particles. The influence of different shapes, like isotropic spherical and anisotropic cubic nanocrystals, is investigated, too. For this study space resolved selected area electron diffraction (SEAD), as well as depth resolved x-ray wide angle diffraction experiments, which
average over a large volume, are used to allow an estimate of any preferred orientation present in the sample. The possibility of manipulating the system during the process of self-assembly and thus a better control of the resulting structure is a desired goal of these experiments.

The influence of spherical and cubic shaped nanoparticles on preferred orientations of the nanoparticle atomic structure during the growth inside the 3D assemblies can be investigated by SEAD on a local area in the superstructure. The sample consists of one mesocrystal, which is cut perpendicular to the substrate surface to a lamella with a film thickness of around 1-2 nanoparticle layers (see real space images figure 4.33a and figure 4.33b). The SEAD images are taken from about a 10x10 nanoparticle cluster of the mapped mesocrystal. The white arrow with the letter n indicates the growth direction of the mesocrystal and is the normal to the substrate’s surface.

The mesocrystal, built up by spherical nanocrystals and self-assembled in an out-of-plane oriented field of 2mT, shows a SEAD pattern with a weak ring structure and clearly visible texture. All reflexes are visible indicating that the single particles are randomly oriented inside the mesocrystal. The intensity on the rings is not equal as the number of illuminated particles is limited. An influence of a weak magnetic field on the orientation of the crystallites during the self-assembly of isotropic spherical nanoparticles is not visible. In contrast, the mesocrystal built up by cubic nanoparticles and self-assembled without any field, shows a SEAD pattern with clearly visible reflections. The electron diffraction pattern shows a 4-fold axis indicating an alignment of the nanoparticles inside the mesocrystal in [100] direction with respect to the beam and for the growth direction an equivalent [001].

For an investigation of existing preferred directions of the nanoparticles inside the mesocrystals with larger statistical relevance, x-ray diffraction measurements with a geometry as shown in figure 2.5 are used. With this method it is possible to average over a wide area and depth of an ensemble of mesocrystals, which allows the observation of out-of-plane aligned lattice planes. The \( \omega - 2\theta \) scans from 0\(^\circ\) to 100\(^\circ\) scattering angle for formations with spherical and cubic building blocks are plotted in figure 4.34. The small angle region, which is shown as inset on the left side, is used to characterize the nanoparticle superstructure and looks very well for both samples. The insets on the right side show the zoom of the interesting wide angle part for the investigation of the preferred crystalline structure orientation.

The scan for the spherical nanoparticles shows all allowed reflections, which have enough intensity to be above the instrument and substrate background, with \( \approx \) the ratios expected (figure 4.34a). This result demonstrates that the crystalline orientations inside the mesocrystals of the ensemble are powder like and nothing indicates a preferred orientation, confirming the observation of the SEAD investigation by TEM on an equivalent sample. Both, the local view on one mesocrystal and the averaged investigation on an ensemble of mesocrystals show no favored crystalline orientation. Independently, the observed peaks exhibit a small shift against the expected positions from bulk, which increase with higher Q values and thus indicate a slightly different crystal lattice in the nanoparticle. In this case a lattice constant which is 0.09% bigger than in bulk maghemite, published with 8.356 Å [72], is found. A lattice strain is a typical observation in nanometer sized particles, specifically the increase of the lattice constant was already observed for small nanoparticles in [103].

The system with cubic nanoparticles exhibits a larger lattice constant of the nanoparticle structure than the maghemite bulk material as well, in this case of 0.2%. In contrast to the spherical
4.2 Self-assembly of 3D ordered nanoparticles

**Figure 4.34:** X-ray diffraction measurements of an ensemble of mesocrystals with different building blocks. The $\omega - 2\theta$ scans run from $0^\circ$ to $100^\circ$ scattering angle and are shown in the overview plot. The small angle part (inset on the left side) shows the good structure of the nanoparticle superstructure, while the wide angle part (inset on the right side) is sensitive to the atomic structure of the particles inside the mesocrystals and illustrates the alignment of the crystalline orientation inside the mesocrystals averaged over the ensemble. The black indices correspond to the $\gamma$-Fe$_2$O$_3$ crystal lattice, the gray one for silicon reflexes from the substrate (spheres: (400) Si reflex; cubes: (111), (222) and (333) Si reflexes; all reflexes produce multiple peaks due to other wavelength contamination in the X-ray beam).
system it features two clearly visible peaks in the wide angle range. These reflexes are indexed as (004) and (008) of the $\gamma$-Fe$_2$O$_3$ structure and show together with the absence of any other reflection (even stronger ones) definitively the presence of a preferred alignment of the nanoparticle structure [001] to the [001] direction inside the mesocrystals, which is parallel to the substrate normal. This observation is consistent with the SEAD experiment. Oriented and randomly aligned crystals have the same peak width in a $\omega/2\Theta$-scan, but the parallel aligned particles all contribute to the same reflections and thus lead to higher intensities.

To quantify the degree of alignment in this sample, a 4-circle X-ray diffractometer was used with more degrees of freedom for the sample positioning (section 3.8). In the configuration used a $\chi$-scan, which is a Q-scan in tangential direction ($\parallel$ to $Q_y$ without changing of $|Q|$), is measurable. Scans are performed on the (004) peak, which was found with the reflectometer, and symmetric positions close to the expected peak positions for comparison (see figure 4.35). The $\chi$-scan on the (004) reflex shows a clear peak, while the other scans have no features at this position. Certainly a preferred crystalline orientation in the [001] direction of the nanocrystals inside the mesocrystals with cubic building blocks is confirmed. Although the particles obviously tend to orient themselves within the mesocrystal lattice, it is impossible to prove the orientation inplane due to the arbitrary orientation of the mesocrystals. The increased intensity of the scan around (0 0 4.14) to lower $\chi$ values is no reflex of $\gamma$-Fe$_2$O$_3$ structure, but background from the substrate. A Gaussian fit on the (004) peak at $\chi_0 = 89.89$ yields a peak width $\sigma$, which describes a random variation of the tilting of the crystalline preferred orientation of the nanoparticles away from the substrate surface normal, of 5.5°. The instrumental resolution of this setup is better than 0.1° and therefore can be neglected for the analysis. Noticeable is that the in-situ
GISAXS experiments show a random variation of the tilting of the c-axis of the nanoparticle superstructure away from the substrate surface of up to 5° (see section 6.3.3). This comparison shows how strongly the particle orientation is defined by the mesocrystal crystal lattice as there seems to be no measurable misalignment of the crystalline to the MC lattice, which would lead to a broadening of the diffraction peak with respect to the GISAXS results.

This series of experiments shows a dependence of the preferential orientation of the nanoparticle structure on the morphology of the building blocks. The system with spheres show no preferred orientation, as expected from their isotropic shape and as only a small field of 2 mT was applied during the process of self-assembly. The field is too low to overcome the thermally activated Brownian motion to align the easy axis in field direction. Applying a much stronger field can actually orient spherical particles, as has been shown in [55, 73]. The van der Waals dominated self-assembly of the spheres has no anisotropy or additional force which could lead to an energetically favorable alignment of the crystalline structure. The anisotropic cubes, on the other hand, exhibit a shape anisotropy which leads by the van der Waals dominated self-assembly to a face-to-face configuration (see section 4.2.4.1), and thus to an alignment of the cubic nanoparticles to the mesocrystal lattice, as one would expected from the structure given. The experiment shows further that the particle facets are always aligned in the [100] directions.

4.3 Conclusions

The process of self-assembly, where the nanocrystals spontaneously order in a superstructure, is a promising way for the fabrication of 3D highly ordered nanoparticle assemblies, so called mesocrystals. In this chapter the post deposition properties of the self-assembly have been investigated for different experimental conditions during the self-assembly. The gathered expertise can be used to develop a better self-organization procedure and tune the resulting parameters of the samples.

The good quality of the γ-Fe₂O₃ particles used, which is an important prerequisite for further experiments, is demonstrated and the newly developed rounded cubes form factor is successfully applied to the measured SAXS pattern. The results from this model of the particle shape have been verified by real space TEM images.

The feasibility of tuning the ensemble of mesocrystals grown by external preparation parameters such as shape, field and evaporation time is proven. For this investigation the combination of complementary microscopy and scattering methods is used to get a full overview over this complex system.

The mesocrystal structure is mainly influenced by the shape of the nanoparticles. No other preparation parameter varied in this work leads to changes in the space group. The determination of the nanoparticle superstructure is consistent with previous experiments [35, 103]: Cubes form a bct structure resulting from the maximization of the van-der-Waals interaction between facets and truncated edges of surrounding particles [86], while the spheres organize in a slightly deformed fcc superstructure due to an interplay of steric repulsion and van-der-Waals interaction, leading to an energetically more favorable fcc than hcp stacking [26, 50, 95]. Additionally, the nanoparticle shape influences the preferred crystalline orientation of the nanoparticles inside the mesocrystals. The anisotropic cubes order with a preferential crystalline orientation of the nanoparticles in the [001] direction parallel to the substrate normal, while isotropic spheres lead
to no preference under the used preparation conditions. An influence of the weak applied field is not visible.

The dependence of the long range order of the nanoparticle superstructure on an applied field during the self-assembly [14, 24, 33, 84] was confirmed in this chapter and examined in dependence on the strength and direction of the field and field gradient. An external field of medium strength (80 mT, 18 mT/cm) applied in the growth direction supports the self-assembly and improves the quality of the ensemble of mesocrystals, while other orientations worsen the result. A good growth of the mesocrystal without any field has to be mentioned, which is in contrast to previous studies by Pileni et. al. [73]. With a field of medium strength the process of self-assembly is still dominated by the van der Waals force and not by the dipole-dipole interaction. For shorter evaporation times the field influence becomes stronger. In general, a longer drying time has a positive influence on the mesocrystal growth as has been reported earlier [33, 38].

Extraordinary conditions for the self-assembly parameters lead to strong alterations of the resulting structures. A multicomponent nanoparticle solution consisting of spheres and cubes self-assembles shape selective in perfectly separated 3D ordered mesocrystal systems. In contrast to previous experiments of the study of shape selective self-segregation [24, 60, 64, 67, 86], the depth resolved GISAXS method is used in addition to microscopy methods, allowing the differentiation between a 2D and 3D ordered structure averaged over the sample and thus a more precise classification of different structures. This is the first detailed investigation of well separated 3D ordered structures within one sample. Using a magnetic field configuration with higher field strength/gradient during the drying of the droplet, a macro-polycrystal (a "bullet"-shaped solid assembly) with a size in the mm-range has been grown, which is visible by the naked eye and consists of clusters of ordered nanoparticles. In this case the dipole-dipole interaction is the driving force to form structures along the field lines.

From the combination of the different results, it has been found that the mesocrystal growth within a broad range of deposition conditions is a size and shape selective ordering process dominated by the van der Waals force taking place in a dense solution at a defined nucleation area. Comparison to the atomic crystal growth of thin films shows many similarities, but mesocrystals feature some new aspects due to the distribution of size and shape of nanoparticles. The experiments realized and their interpretation with respect to the mechanisms of self-organization provide the first components for a model of the mesocrystal growth, which was refined by the results of the following chapters.
Chapter 5

Modeling of scattering intensities of 3D nanoparticle assemblies

In this chapter the quantitative analysis of the different scattering experiments will be discussed in detail. Although it was not possible to simulate most scattering patterns precisely, many of the core features could be reproduced and explained. Besides the experiment dependent difficulties (as e.g. refraction and reflection in GISAS experiments) the principle inhomogeneity of the mesocrystal 2D powder, forming on the substrate during the self assembly, introduces additional complexity to the model and leads to e.g. peak broadening, which masks the "true" physical characteristics of the structural order.

5.1 General considerations

5.1.1 Single mesocrystal structure factor in Born Approximation

Independent on the scattering method, the Born Approximation (BA) is a good starting point to analyze the scattering pattern, as it gives good results even for grazing incidence experiments, when one does not get too close to the critical angle of total reflection. Secondly, the DWBA used in the later case needs a BA structure factor for its calculations.

A single mesocrystal itself is approximately a cylinder shaped crystal of equal particles and the scattering potential \( V_{Meso}(\vec{R}) \) can thus be decomposed into the product of a function describing the cylinder shape \( P_{MC} \) and the regular, infinite lattice convoluted with the nanoparticle scattering potential \( V_{NP} \) (see section 2.2.3). The Fourier transform of this function (structure factor) can be derived using the convolution theorem (eqn. 2.30) as the product of the nanoparticle form factor \( F_{NP}(\vec{Q}) \) with the convolution of the reciprocal lattice and a cylinder form factor \( F_{MC}(\vec{Q}) \):

\[
V_{Meso}(\vec{R}) = V_{NP} \otimes \left( P_{MC}(\vec{R}) \cdot \sum_{uvw}^{N} \delta(\vec{R} - \vec{R}_{uvw} - \vec{r}_{i}) \right)
\]

(5.1)

\[
S(\vec{Q}) = F_{NP}(\vec{Q}) \cdot \left( F_{MC}(\vec{Q}) \otimes \sum_{hkl}^{N} \delta(\vec{Q} - \vec{Q}_{hkl}) \cdot e^{i\vec{Q}\vec{r}_{i}} \right)
\]

(5.2)
where the real space and reciprocal lattice points are defined as \( \vec{R}_{\text{avw}} = u\vec{a} + v\vec{b} + w\vec{c} \) and \( \vec{Q}_{\text{hkl}} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \), respectively. \( N \) denotes the number of particles in the unit cell with a position of \( \vec{r}_i \). The particle form factor for perfectly mono disperse spheres with radius \( r \) is calculated for a 200

For the numeric calculation of the rounded cubes form factor, the density described by equation 5.5 is calculated for a 200\(^3\) points cubic space region, Fourier transformed using FFT and than interpolated (implementation in appendix section B.1). The flat truncation has the analytic solution equation 5.4, which is not defined for zero or equal \( Q \) components and thus needs to be calculated at slightly different \( Q \) positions numerically (see appendix section B.1). The new model can reproduce a perfect spherical and cubic system equivalent to the analytic models showing the applicability of the numeric approximation (see figure 7.16).
5.1 General considerations

The geometric representation of the two different kinds of cubic form factors in real space. The definition and some example values for the degree of truncation \( \tau \) is shown.

![Figure 5.1: The geometric representation of the two different kinds of cubic form factors in real space.](image)

The real space representation of the two kinds of truncated form factors (truncated (flat) and rounded) are sketched in figure 5.1. The truncation parameter \( \tau \) is chosen relative to the edge length \( a_{NP} \) such that 1 corresponds to maximum and 0 to no truncation. The extreme case \( \tau = 0 \) matches for both cases an ideal cube, while \( \tau = 1 \) corresponds to a perfect spherical particle for the rounded cube model and a cubeoctahedron for the truncated cube model.

Equally, one can derive the mesocrystal shape form factor as the FT of a cylinder of radius \( r_{MC} \) and height \( h_{MC} \), with \( J_1 \) as the Bessel function, aligned with the cylinder axis parallel to \( z \) as [71]:

\[
F_{MC}(\vec{Q}) = 2 \frac{\sin(h_{MC}Q_z)}{h_{MC}Q_z} \left( \frac{J_1(r_{MC}\sqrt{Q_x^2 + Q_y^2})}{r_{MC}\sqrt{Q_x^2 + Q_y^2}} \right)
\]  

(5.6)

The scattering intensity is the absolute square of the structure factor and as the particle form factor is a multiplicative factor it can be separated in the intensity equation as well:

\[
I(\vec{Q}) = |S(\vec{Q})|^2 = |F_{NP}(\vec{Q})|^2 \cdot |F_{MC}(\vec{Q})| \otimes \sum_{HKL} \sum_{i=1}^{N} \delta(\vec{Q} - \vec{Q}_{HKL}) \cdot e^{i\vec{Q} \cdot \vec{r}_i}|^2
\]

(5.7)

Equation 5.7 shows clearly, that the individual measured peak intensity is given by the form factor and the sum in the structure factor term \(^1\) while the peak shape is described by the mesocrystal shape form factor. The structure factor term can only be the square of an integer number between 0 and the number of particles in the unit cell \( N \). For the simple systems investigated here, the structure sum is either zero or one/four, so each peak intensity is given by the FF only.

\(^1\) The structure factor term can only be the square of an integer number between 0 and the number of particles in the unit cell \( N \). For the simple systems investigated here, the structure sum is either zero or one/four, so each peak intensity is given by the FF only.
tial shape form factor, which is placed at every allowed reciprocal lattice position. This holds true for a mesocrystal of perfectly equal particles situated exactly at the lattice positions. In a real mesocrystal there will always be a deviation in particle size and position. The positional offset can be treated similarly as in the derivation of the Debye-Waller factor described in section 2.2.4 with the only difference that the positional offset is not averaged over time but over particle positions. This leads to a Debye-Waller term $e^{-\frac{1}{3}|\mathbf{Q}|^2 <a^2>}$ in the intensities and an additional incoherent contribution to the single particle form factor.

Figure 5.2: Cubic particles ordered in on a mesocrystal with deviation of the particle position (SEM picture on top of a mesocrystal).

The positional deviation can be seen in figure 5.2, where some cubic particles are not on the regular grid positions. Describing a variation of particle size is everything but trivial, as these variations will most definitely lead to a local change in lattice constants which introduces additional changes to peak shapes, intensity and incoherent contribution.

If the correlation of the mesocrystal structure is limited, and much smaller than the mesocrystal size, the peak shape described by $F_{MC}(\mathbf{Q})$ approaches a Lorentzian with a HWHM which is related to the correlation length as $\xi = \frac{2\pi}{\text{HWHM}}$.

5.1.2 Influence of 2D powder and mesocrystal ensemble statistics

In general, the samples under investigation consist not only of one single mesocrystal, but also of an ensemble of mesocrystals which grow independently. The ensemble delivers a variety of new properties, which influence the scattering pattern and the probability weighted sum of many individual simulations over the entire parameter range needs to be calculated. These new influences will be discussed in this subsection and are needed to describe the scattering pattern of complex 3D nanoparticle systems.

**In-plane rotation** For all but the single mesocrystal samples, the substrate only provides the surface plane, which defines the direction of the $\hat{c}$-axis, so that there is no preferred orientation of the $\hat{a}$ direction in the plane. The mesocrystals are arbitrarily oriented to each other, a so-called 2D powder. This means that each reciprocal lattice point is associated with a circle in reciprocal space around the $z$-axis. This makes it possible to measure all scattering planes in one orientation of the sample as it was used in all over GISAXS experiments, but it makes the individual lattice directions indistinguishable. As the mesocrystal areal density is in the order of $\frac{1}{(10\mu m)^2}$ compared to a beam size of 0.1-1 mm$^2$ there are $10^4$-$10^5$ mesocrystals in the scattering volume, so one can expect no influence of texture on the peak intensities. This means that peaks originating from completely different scattering planes can still be compared in a GISAS experiment.
5.1 General considerations

(a) SEM picture of an ensemble of mesocrystals. The small points between the huge mesocrystals are crystals in the nanometer range.

(b) An incoherent average of an ensemble of Gaussian size distributed mesocrystals compared to the pure peak shape of a mesocrystal of average size.

Figure 5.3: Influence of size distributed ensemble of mesocrystals on the peak shape.

Independence of mesocrystals  Due to the effect described above there is a very low probability that two neighboring mesocrystals in an average distance of 10 µm are aligned equal enough to produce the same peaks (except for the (00L) type reflections) and thus the mesocrystals, which contribute to the same reflections, will have a distance much larger than the coherence area (≤ 10 µm · 100 nm) of the scattering experiment. Here we assume due to random variations in orientation and position of the mesocrystals coherent scattering between different mesocrystals can be neglected. Thus we calculated the incoherent superposition of scattering from the mesocrystals by adding intensities, not amplitudes. These components were to be add incoherent together as intensities.

Mesocrystal size distribution  As can be seen in the SEM figure 5.3a, the mesocrystals grown have a large size variation between ≈500 nm and ≈20 µm. The incoherent average of an ensemble of Gaussian size distributed mesocrystals is shown in figure 5.3b, compared to the pure peak shape of the mesocrystal of average size. One can see that the shape of the central peak is distorted and the oscillation minima are smeared out. Although this variation is easily introduced into a model it requires recalculation of the complete model several times.

Deviation in shape  The description of the in-plane shape of the mesocrystals as circles is a simplification as is obvious from many SEM images from nanocube samples (see figure 5.4a, 5.4b). Often the mesocrystals are less symmetric, building octagons, rectangles or diamond shapes. For the nanospheres samples the cylindrical model is very close to reality (figure 5.3a, 5.4c). A shape changing over one single sample is observed, too. Although this could change the peak shapes for single mesocrystal experiments (where the preparation automatically leads to cylindric shape) the impact on GISAS measurements is expected to be negligible due to several reasons. The limited resolution of the instrument (e.g. ID01: 0.0054 Å⁻¹) leads to much broader peaks than the theoretical width of the large in-plane size of the mesocrystals (0.00013 Å⁻¹), so any change in fine features would not be detectable. Additionally, the influence of
the nanoparticle size distribution on the peak shapes of the mesocrystal is expected to be much larger.

**Out-of-plane rotation**  Samples produced with shorter solvent evaporation times often show radial smearing of peaks in the GISAXS patterns. Microscopy investigations have shown that some mesocrystals have tilted \( \vec{c} \)-axes with respect to the substrate surface normal (figure 5.4d). In contrast to the equally distributed rotational average of the in-plane component, this is a Gaussian distributed orientational misalignment, which needs to be considered by averaging the model for different rotations. The effect of such a rotational average is shown in (figure 5.5c) as \( \sigma_{\text{tilt}} \).

**Lattice constant deviations**  There can be a distribution of the mesocrystal unit cell geometry in the sample, which leads to different reciprocal lattice vectors and thus peak positions for the different mesocrystals. The simplest form of this distribution is an equal Gaussian variation of all lattice parameters, which leads to a radial smearing of the peaks as shown in (figure 5.5c) as \( \sigma_r \). This is not always sufficient to describe the peak shape if the in-plane lattice constant variation is different from the out-of-plane one. In this case the directions need to be treated independently.

**Computational challenges**  Unfortunately all of the situations above can be found combined in one sample, which requires the computational average over 3-5 variables. Even for an extremely low sampling of 10 points per variable this would lead to thousands of model evaluations. For a full modeling of a GISAXS pattern with about \( (1024 \text{ pix})^2 \) and a peak function which takes only 100 CPU operations (it is a high level function of complex variables) this leads to \( 10^4 \cdot 1024^2 \cdot 100 = 10^{12} \) operations taking about 5 minutes on a modern system. When the model function gets more complex this can increase drastically, making the model impractical or even useless. Some of the averages can also be described as a convolution of two simple functions which makes it possible in special cases to use a fast Fourier algorithm to compute the peak shapes, which reduces the evaluation times by several orders of magnitude (fast Fourier transform (FFT) convolution is \( O(n \cdot \log(n)) \) compared to \( O(n^2) \) of a summation).
5.1 General considerations

(a) Mesocrystals with cubic building blocks observed close to the edge of the sample (LM picture).

(b) Mesocrystals with cubic building blocks observed more in the center of the sample (LM picture).

(c) Mesocrystals with spherical building blocks (LM picture).

(d) Mesocrystals with cubic building blocks, which are tilted (SEM picture under 45°).

(e) Mesocrystals with cubic building blocks and high density (SEM picture).

(f) Mesocrystals with cubic building blocks with large distance (SEM picture).

Figure 5.4: The complexity of the mesocrystal ensemble is shown as examples in these SEM and LM pictures. The shape deviation is illustrated in figure 5.4a, 5.4b and 5.4c, in which figure 5.4a and 5.4b exist in one sample. Figure 5.4d is an example for the out-of-plane rotation which is observed. The variation of the mesocrystal distances is shown in figure 5.4e and 5.4f.
5.2 Grazing incidence specific considerations

In scattering experiments at grazing incidence, the incoming or outgoing beam approaches the critical angle of total reflection of the substrate (and mesocrystal film). Close to this angle the beam is refracted when penetrating the material and partly reflected at the surface. The simple BA is no longer valid as the approximation of weak scattering no longer holds. When considering only the specular reflected beam intensity this can be described by an optical approach based on Parratt’s formalism (see section 2.2.5). When other scattering geometries (in-plane GISAS, off-specular scattering) are considered, the distorted wave Born approximation combines the refraction and reflection effects of the optical approach with the Born approximation to describe scattering from structures in the surface plane (see section 2.2.5).

5.2.1 Substrate reflection

As most GISAXS experiments are performed close to the critical angle of the substrate there is a considerable part of the beam reflected from the surface. This reflected beam can also be scattered from the nanoparticles above the substrate surface which leads to additional "reflected" peaks. Although these peaks have been observed in some experiments they are in our case \((\alpha_i > \alpha_c)\) much weaker than the directly scattered ones and thus do not impact most quantitative studies. Anyway, this effect is introduced in the DWBA based models.

5.2.2 Refraction

The ordered nanoparticles themselves can be seen as a separate layer on top of the substrate. When the beam penetrates this layer (or leaves the layer after scattering) it is refracted, is slightly changed the incident (or outgoing) beam direction. This effect leads to a slight \(Q_z\) shift of reflections. Considering Snell’s law when calculating the scattering vector inside the material this shift can be deduced [27] to:

\[
Q_{z,\text{observed}} = k_0 \left( \pm \sin(\alpha_i) \pm \sqrt{\left\{ \sin(\alpha_{\text{Mes}})^2 + \left( \frac{Q_z \cdot \lambda}{2 \cdot \pi} \pm \sqrt{\left( \sin(\alpha_i)^2 - \sin(\alpha_{\text{Mes}})^2 \right)^2} \right\}} \right) \tag{5.8}
\]

In this formula \(\alpha_{\text{Mes}}\) is the critical angle of the mesocystal layer and \(Q_z\) the momentum transfer component in the layer perpendicular to the surface. This shift is considered when fitting the peak positions to deduce the correct mesocystal lattice parameters from the experimental data.

5.2.3 Inhomogeneity

The considerations above are usually applied to layered systems or continuous films of particles/polymers. In the case of the mesocrystal samples one faces additional obstacles as there are no closed layers of ordered particles (see figure 4.10). At the center of a mesocrystal there is a
5.3 Model implementation

thick layer of large density leading to strong refraction effects, at the edge the density is lower and between mesocrystals there are no particles or a thin layer of one or two particles, where the reflection from the substrate becomes more important. If the distance between the mesocrystals would be much smaller than the in-plane coherence length, these effects would lead to an average density profile, while a mesocrystal distance much larger than the coherence length could be modeled by incoherent summation of these three regions. The mesocrystal sizes/distances vary widely from 100/500 nm to 10/100 µm for different samples (see figure 5.4e, 5.4f) and even on different regions of the same sample. Unfortunately the intermediate situation is found for most samples and it is not clear prior to modeling how much incoherent summation is needed.

In addition to the lateral inhomogeneities, vertical ones are present in the ensemble of mesocrystals as well. A variation of heights of different mesocrystals leads to an \( \alpha_{\text{Meso}} \) distribution and thus a distribution at \( Q_z \) shift’s, which results in smeared out peaks, especially in the low \( Q_z \) region. A broad Yoneda line is an other consequence of this inhomogeneity. Additionally a gradient of lattice constants increasing with height has to be assumed to accurately describe the Bragg-peak positions.

5.3 Model implementation

5.3.1 Single mesocrystal modeling

For the single mesocrystal diffraction measurement in chapter 7 the data is described with the simple model given in eqn. 5.7 with an additional Debye-Waller factor term representing the lattice position deviation. The peak shape and the Laue oscillations are introduced well by the mesocrystal shape, wherein the preparation automatically leads to a cylindric shape of the isolated mesocrystal. Variations of the particle size are not considered. The good agreement of this simple model with the measured data can be seen in figure 7.9 and in appendix chapter B. The python script is attached in appendix section B.3.

5.3.2 Peak shape computation for in-situ experiments

In these experiments there was no sign of oscillations between the main peaks, due to an average over different mesocrystals of the ensemble. The experimental intensities were divided by the single particle form factor before fitting selected peaks. Thus in this model, the mesocrystals diffraction pattern is analyzed without consideration of grazing incidence. The DWBA \( T_f, R_f, T_i, R_i \) terms are negligible as there is no sign of reflected peaks and because the peak positions lie well above the Yoneda line. Additionally an averaged background correction was done for every picture before the fit. These two corrections make stable fits possible, not altered by the slopes of the FF.

The peak shapes were created by FFT convolution of a 2D Lorentzian (mesocrystal correlation) with 2D Gaussian (orientation and radial \((a^*, c^*)\) average) and an experimental shape function.
Chapter 5 Modeling of scattering intensities of 3D nanoparticle assemblies

(a) Beam-shape  (b) 2D Lorentzian  (c) Radial Gaussian

Figure 5.5: The three components used to compute the peak shape with FFT.

The beam shape function (eqn. 5.9 and figure 5.5a) consisting of a step with exponentially decaying edges was used to model the finite beam size and the crosstalk of neighboring pixels.

\[
B(x) = \begin{cases} 
  e^{(x-w^2)/d}, & \text{if } x < -\frac{w}{2} \\
  e^{(w^2-x)/d}, & \text{if } x > \frac{w}{2} \\
  1, & \text{else} 
\end{cases} \tag{5.9}
\]

The beam shape function parameters were obtained by fitting to a specular reflection of the clean silicon substrate. To model the mesocrystal correlation length \((\gamma_x, \gamma_y)\) a 2D Lorentzian function (eqn. 5.10 and figure 5.5b) was used.

\[
L(\vec{Q}) = \frac{I_0}{1 + (\frac{Q_y}{\gamma_y})^2 + (\frac{Q_z}{\gamma_z})^2} \tag{5.10}
\]

Finally, a random variation of the mesocrystal lattice parameters and tilting of the c-axis away from the substrate surface can be described by a 2D Gaussian function in polar coordinates of the radial \(\sigma_r\) and tangential \(\sigma_t\) position (eqn. 5.11 and figure 5.5c).

\[
G(\vec{Q}) = e^{-\frac{1}{2} \left(\frac{Q_r-r_0}{\sigma_r}\right)^2} \cdot e^{-\frac{1}{2} \left(\frac{\phi-\phi_0}{\sigma_t}\right)^2}, \text{with } Q_r = \sqrt{Q_y^2 + Q_z^2}, \phi = \arctan\left(\frac{Q_z}{Q_y}\right) \tag{5.11}
\]

The refraction formula eqn. 5.8 was used to correct the measured peak positions in consideration of the DWBA. Fits of 6 different peaks and their \(-Q_y\) mirror pairs with coupled parameters were performed yielding the reciprocal lattice parameters, in-plane and out-of-plane correlation length and distribution widths. This simple model was sufficient to describe most of the measured peak shapes and was still applicable to fit several hundred of GISAXS images automatically. The good agreement of the fit functions to the measured data is exemplified in figure 6.7. A multicore implementation of this function can be found in appendix section B.4.
5.3 Model implementation

Figure 5.6: Sketch of the model for the particle density at a given position and the different parameters used in eqn. 5.12-5.14. For the case of closed packed spheres and body centered tetragonal cubes the model parameters indicated are: Position of the model slice $z$, individual particles $z_i$, spheres radius $r$, cubes edge length $a$ and unit cell cross section $S_{UC}$.

5.3.3 Reflectivity modeling

For reflectivity the largest difficulty is to describe the scattering length density well enough to reproduce the unusual peak shapes. Simple layer models trying to implement all influences of the mesocrystal ensemble statistic described above get very complex, easily introduce 20 or more free parameters and still are not able to explain the full reflectivity curve including the total reflection region. The lateral inhomogeneity described above must be considered as well to describe the underlying long oscillations properly as they originate from the single particle layer between the mesocrystals.

A modified version of the GenX program [25] was used to include the incoherent averaging procedure, as most reflectivity programs do not consider this possibility. A new approach was tried, calculating density profiles from the particle shapes and positions while in a second step creating a fine layered model for the reflectivity simulation.

$$\rho_{UC}(z) = \left( \rho_{Fe_2O_3} - \rho_{Matrix} \right) \frac{\pi \sigma^2 - (z-z_i)^2}{S_{UC}} \quad (5.12)$$

$$\rho_{UC}(z) = \left( \rho_{Fe_2O_3} - \rho_{Matrix} \right) \frac{\sum a^2, \text{for } |(z-z_i)| \leq a/2}{S_{UC}} \quad (5.13)$$

$$\rho_N(z) = \rho_{Matrix} + \sum_{j=0}^{N} \rho_{UC}(z - c \cdot j) \quad (5.14)$$

$N =$ repetitions of unit cell
This method typically uses 20-40 layers to calculate the reflectivity with the Parratt’s formalism (see section 2.2.5) for each mesocrystal unit cell while keeping the number of parameters to only 5 to 8 for the whole mesocrystal. This model is than calculated for different lateral particle densities to describe the center of a mesocrystal, the edges and the region in between the mesocrystals, summing up the intensities afterwards as described in equation 5.15.

\[
I_R = S_{\text{free}} \cdot I(\rho_1(z)) + S_{\text{edge}} \cdot I(\rho_1(z) + 0.5 \cdot \rho_N(z)) + S_{\text{center}} \cdot I(\rho_N(z)) \tag{5.15}
\]

\[
S_{\text{edge}} = (1 - S_{\text{free}}) (\frac{(R_{\text{Meso}} + R_{\text{Coherence}}/2)^2 - (R_{\text{Meso}} - R_{\text{Coherence}}/2)^2}{R_{\text{Meso}} + R_{\text{Coherence}}/2}^2)
\tag{5.16}
\]

\[
S_{\text{center}} = (1 - S_{\text{free}}) (\frac{(R_{\text{Meso}} - R_{\text{Coherence}}/2)^2}{R_{\text{Meso}} + R_{\text{Coherence}}/2}^2)
\tag{5.17}
\]

using the symbols: \(UC\)-Unit Cell, \(\rho\)-Scattering power density, \(S_{\text{UC}}\)-Unit cell cross section area, \(I(\rho(z))\)-Simulated intensity for a given scattering power density profile, \(S\)-Relative surface occupation, \(R\)-Cylinder radii as sketched in figure 5.7. To account for mesocrystals with reduced radius from bottom to top the segmentation of the outer region is increased and the particle density from bottom to top is decreased for the edge regions. To simplify the formulation of the relative size calculation of the coherence and mesocrystal areas, both are taken to be circles in this model. In the experiment the coherence volume is strongly elongated in the beam direction, but has an area that is smaller than most mesocrystals (≈100 nm x 10 µm).

The different parts of this model are exemplified in figure 5.8 together with the combined intensity. The center part describes a perfect mesocrystal with full density and thus showing strong maxima and low minima. The edge zone has a lower averaged density and produces a lower contrast. The mono layer between the mesocrystals (free) creates an underlaying long oscillation. The combination of all three components in addition with a deviation of lattice constant in one mesocrystals produce the resulting pattern.

Although this model fits the experimental x-ray and neutron data at higher Q values quite well the total reflection region below 0.04 Å\(^{-1}\) in the x-ray case is not reproduced perfectly, most likely due to too much simplification of the inhomogeneity over the sample surface and missing interference terms from the different surface areas. In this routine an average mesocrystal size in height and diameter, as well as an average model for the coverage of the sample with the different density regions is used. An additional integration of a lattice constant variation for the substrate to the surface of the MC was introduced to properly fit the shape of the Bragg peaks. Although the model uses some generalizations and does not include size, height and shape deviations it is already very complex, especially from the implementation and calculation point of view (see code in appendix section B.5.). For example the influence of different mesocrystal sizes can lead to different densities (\(\alpha_c\)'s) and thus to a smeared out total reflection edge. This
5.3 Model implementation

Figure 5.8: Example of simulated reflectivity with each sub-model. The red labels describes the X-ray data and the blue one correspond to the neutron data. The black points are the measured data. Edge, free and center correspond to the parts referred to as $S_{\text{edge}}$, $S_{\text{free}}$, $S_{\text{center}}$ in eqn. 5.15-5.17, the contribution of the different regions of the mesocrystal. Full is the weighted sum of all components $I_R$ from eqn. 5.15. The sample is an ensemble of mesocrystals formed with extra long waiting time from spherical building blocks of radius 5.01 nm self-assembled under an magnetic field of 2 mT and gradient up. The measurement was done with a wavelength of 4.73 Å for neutrons and 1.54 Å for X-rays.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{\text{bottom}}$ [nm]</td>
<td>9.8</td>
<td>2</td>
</tr>
<tr>
<td>$c_{\text{top}}$ [nm]</td>
<td>9.2</td>
<td>7</td>
</tr>
<tr>
<td>$r_{\text{NP}}$ [nm]</td>
<td>4.9</td>
<td>7</td>
</tr>
<tr>
<td>N</td>
<td>40</td>
<td>/</td>
</tr>
<tr>
<td>$R_{\text{Meso bottom}}$ [nm]</td>
<td>3630</td>
<td>500</td>
</tr>
<tr>
<td>$R_{\text{Meso top}}$ [nm]</td>
<td>670</td>
<td>500</td>
</tr>
<tr>
<td>$R_{\text{coherence length}}$ [nm]</td>
<td>1500</td>
<td>/</td>
</tr>
<tr>
<td>surface filling ratio [%]</td>
<td>47</td>
<td>7</td>
</tr>
<tr>
<td>magnetic moment per formula unit $\mu_{\text{Bohr}}$</td>
<td>0.98</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.1: Fit parameters used for the simulation shown in figure 5.8.
Chapter 5 Modeling of scattering intensities of 3D nanoparticle assemblies

(a) GISAXS measurement  
(b) GISAXS simulation

**Figure 5.9:** BornAgain simulation of the GISAXS scattering intensity of an ensemble of mesocrystals formed with long waiting time from spherical building blocks of radius 5.01 nm self-assembled under a magnetic field of 80 mT and gradient up. The measurement was done under an angle of 0.4° and with a wavelength of 1.77 Å at SWING/Soleil.

is not so prominent in the neutron case as the absorption can be neglected and the total reflection is dominated by the substrate.

### 5.3.4 Lógos and BornAgain (work in progress)

In the GISAS case the problem gets more complex as in addition to the layer density, the in-plane structure needs to be taken into account in the DWBA formalism. For both directions the influence of the mesocrystal ensemble statistics and their averages have to be considered. The DWBA implementations Lógos and BornAgain (developed together with the scientific computing group in the JCNS outstation at MLZ and Artur Glavic) of the model up to now does not incorporate surface inhomogeneity (explained in the reflectivity part) and thus only describes one homogeneous layer of average particle density. The model includes via eqn. 5.7 the mesocrystal structure and shape ($F_{MC}(\vec{Q})$), the in-plane rotation (2D powder), distribution of mesocrystal size, Debye-Waller factor (deviation of lattice positions), refraction and reflection as well as the nanoparticle form factor. An example simulation is shown in figure 5.9b and the fit results in comparison to experimental determined parameters match well (table 5.2).

The mesocrystal structure provides the peak positions, the mesocrystal shape FF together the peak shape and the particle FF with the structure factor the peak intensity. The 2D powder allows one to see different scattering planes at once. The size distribution of the mesocrystals leads to a smearing out of the Laue-oscillations and the Debye-Waller factor to a decay of intensity for larger |Q|. Although this model already describes some datasets quite well, the Yoneda region and peak broadening are not well reproduced. As the reflectivity model shows, it is important to include several aspects of the surface inhomogeneity to describe the total reflection and thus the Yoneda region correctly. The incorporation of all regions and different sizes will give a distribution of critical angles and thus a broadening of the Yoneda line. The integration of out-of-plane rotations and lattice constant deviations would induce the tangential and radial broadening of the peaks.
5.4 Conclusions

Modeling of scattering intensities of an ensemble of 3D nanoparticles is introduced in this chapter and shows the good understanding of the system under investigation. The complexity of the mesocrystal samples represents a challenge for the simulation from physical and numeric perspectives. Simplifications in experimental or theoretical conditions, like investigation of a single 3D mesocrystal or an approximation by consideration of a special case, yields good agreement with experiments. If we consider the complete ensemble of mesocrystals and the full scattering pattern, the number of features increase and with them the free parameters and elements in the model. Although the simulations and fitting were not carried out until perfect agreement, the successful understanding of the underlying physics is evidenced. The possibility to deduce the influences of the 2D powder and the mesocrystal ensemble statistics, like in-plane rotation, mesocrystal size distribution, shape deviation, out-of-plane rotation, lattice constant deviation, lateral and vertical inhomogeneities and the space group, gives a new aspect of interpreting reflectometry and GISAS data. A new form factor model complements the study to allow a more precise fitting of different scattering experiment datasets.

<table>
<thead>
<tr>
<th>parameters</th>
<th>fit parameters</th>
<th>experimental parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>a [ nm ] :</td>
<td>12.4</td>
<td>12.7 ± 0.1 (GISAXS)</td>
</tr>
<tr>
<td>c [ nm ] :</td>
<td>30.2</td>
<td>31.3 ± 0.1 (GISAXS)</td>
</tr>
<tr>
<td>r_{NP} [ nm ] :</td>
<td>4.7</td>
<td>5.01 ± 0.02 (SAXS)</td>
</tr>
<tr>
<td>σ_{r_{NP}} [%] :</td>
<td>8</td>
<td>6.3 ± 0.5 (SAXS)</td>
</tr>
<tr>
<td>height_{Meso} [ nm ] :</td>
<td>112</td>
<td>250-500 (AFM)</td>
</tr>
<tr>
<td>radius_{Meso} [ μm ] :</td>
<td>0.9</td>
<td>1.5-3.5 (SEM)</td>
</tr>
<tr>
<td>surface filling ratio [%] :</td>
<td>17</td>
<td>23 ±2 (AFM)</td>
</tr>
<tr>
<td>roughness :</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>beam intensity :</td>
<td>5.01·10^{12}</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Fit parameter used for the simulation shown in figure 5.9b.

The influence of e.g. out-of-plane rotation could be implemented, although at the cost of longer computation time, which already is in the order of minutes for a single scattering pattern.
Chapter 6

Time evolution of mesocrystal growth

The self-assembly of magnetic nanoparticles has a high potential for future applications [63], as it allows mass production processes of very small structures without the use of expensive equipment. The process itself is complex, including several interactions between nanoparticles, solvent and substrate. A deeper understanding is the key for a better control of the self-organization, which subsequently can be used to develop better self organization procedures and tune the resulting parameters of the sample. Previous studies investigated the self-assembly of non-magnetic particle systems [21, 22, 28, 53, 65, 76, 92, 93], spherical superparamagnetic nanoparticle monolayers [82, 83] or nonspherical particle systems like cubic [29] or nanocathedral [98]. Most of the observed self-assembling process can be classified into the following groups: The ordering takes place at the liquid-air interface [22, 28, 53, 65, 92, 93] or at the triple phase contact line (substrate-liquid-air) [76, 82, 83]. The in-situ GISAXS technique has been established as a good choice for real time investigations of the ordering at the nanometer scale [49, 75].

In this chapter, an in-situ GISAXS study of highly ordered 3D nanoparticle assemblies is discussed. In contrast to earlier studies we have focused our investigation on the evaporation-induced 3D growth of spherical and cubic magnetic particles, which form a highly correlated system. Our main focus was to observe the influence of different evaporation times on the growth mechanism and to measure the very early assembly stages. To achieve a better insight into the self-organization process compared to earlier experiments, an additional apparatus was installed which recorded different parameters simultaneously with the GISAXS information and a more quantitative time dependent analysis of the GISAXS patterns was carried out. The main scientific question addressed with this study is where, when and how the assembly does take place. The following pages treat these questions and give a new insight into the evolution of mesocrystal growth from magnetic nanoparticles.

6.1 Development of the in-situ cell

For our in-situ SAXS and GISAXS experiment we designed a new evaporation cell with several features for the control of the self assembling parameters. The dimension was restricted by the available space at the ID01 beamline at ESRF (see section 3.7) to less than 10 cm in beam direction. The setup was designed to be similar to the conventional drop casting, as done in a Petri dish. The cell (figure 6.1) consists of a glass body with gas inlet/outlet valves (a) and a glass cover plate (b). Two Kapton windows (c) allow transmission of the x-ray beam and two
flat windows (d) offset by 30° against the x-ray beam axis transmit light from the attached light band micrometer (e) to measure the droplet height. Additionally a microscope camera (f) observes the sample surface under an angle. The magnetic field is produced by permanent magnets that can be inserted into the body holder (g) or on top of the cover plate (b). The evaporation rate is controlled by the air inlet/outlet through the valves and by an additional symmetric toluene reservoir inside the cell.

In the following the former features are described in more detail:

- Kapton windows, allowing x-rays to enter/exit the cell without too much intensity loss (85% transmission). The size of these windows are 30 x 17 mm². They enable a large scattering angle in forward scattering of up to 16°, which corresponds to a Q value of 2.74 Å⁻¹ at the used wavelength. This is more than adequate for our scattering experiment.

- A light-band micrometer from Keyence® was used to measure the height of the droplet during the experiment. The system consist of a strong diode with a line shaped green ray that shines on the sample horizontally and the shadow cast by the droplet is detected with a high resolution camera. It was tested with several solvents to be able to measure the height through the glass setup with a precision of 0.1 μm. This precision in combination with the scattering makes an identification of the position of the mesocrystal growth possible. Additionally an exact starting time for the experiment could be defined. An advantage of this method is the independence from the solvent (for example the refractive index which influences a fill metric sensor). The Light-band micrometer system was connected with a computer outside the measurement hutch and recorded with a time code to correlate it to the x-ray images taken. The micrometer was tilted to the beam, as well, to fit inside the residual space.
6.2 Experimental details

The microscope camera was used to monitor the droplet size from an angle to be able not only to see the height of the droplet but also its in-plane coverage. It was also connected to the computer outside the measurement hutch and the images were saved with a time code.

Applying a magnetic filed is important for the deposition process (see chapter 4). The influence of the magnetic field (strength and direction) on the self assembling process can be controlled in this setup, as well. A permanent magnet with a steel plate on the back was placed on top of the in-situ cell, producing a field gradient pointing away from the substrate $H_{\perp}$ with 36 mT field strength at the sample position. For a field gradient pointing to the substrate $H_{\parallel}$, a permanent magnet was included inside the holder body (g) and reached a field of 65 mT. A homogeneous magnetic field in out-of-plane direction $H_{\uparrow}$ with a field strength of 100 mT could be reached with both magnets at once. An in-plane filed $H_{\sigma}$ of 30 mT can be applied using two magnets on opposite sides on top on the toluene vessel, too.

For a better control of the evaporation, small symmetric openings allow gas exchange (solvent<->air), which can be controlled with valves. Varying openings change the evaporation rate of the toluene and allow a precise control. Additionally a symmetric solvent reservoir can be used to slow down the evaporation rate. It is surrounding the sample stage and can be filled with different amounts of toluene. This way the reservoir could be used to control the evaporation rate as well as saturate the atmospheres already before adding the solution and gave us the possibility to leave the hutch and start the measurement without missing important stages.

6.2 Experimental details

The cell was mounted at the sample position of the ID01 beamline (figure 6.2) and aligned with a silicon wafer using the reflected beam. The flight path was evacuated up to a few cm before
Chapter 6 Time evolution of mesocrystal growth

Figure 6.3: Different geometries used at ID01 beamline

and after the cell to minimize air scattering. The best available focus of 30x1000 μm² was set to achieve a small footprint on the sample, which is necessary to define the observed region. Two different geometries have been used, a transmission SAXS geometry (figure 6.3a) with the substrate parallel to the incident beam as long as the droplet was larger than the beam height and a standard GISAXS geometry (figure 6.3b) with 0.3° and 0.6° angle of incidence. The 0.6° setting was not used for a short evaporation time experiment. The SAXS geometry allows the detection of ordered clusters within the solvent and at the solvent surface. As the transmission geometry was measured with a fine vertical focus it allowed us to scan the beam through the liquid during evaporation (not possible for short evaporation time). Nucleation at the bottom could be detected in this configuration, too. The GISAXS geometry is mostly sensitive to particles ordered at the substrate surface and is applied after the droplet has a minimal height between 20-50 μm measured by the light-band micrometer. So we could assure not to miss the beginning of the nucleation on the substrate.

The sample handling and preparation for the in-situ experiment was done with the conventional preparation process as described in section 4.2.1. For all deposited samples the standard solutions $S^8_8$ and $S^8_4$ were used. The preprocessed wafer was inserted into the cell, covered with a cap and every substrate was aligned with the silicon reflection for its position and angle. The zero position of the micrometer was set with the substrate shadow afterwards. Depending on the required evaporation speed, a defined amount of toluene was put in the reservoir to achieve the desired degree of saturation of toluene in the atmosphere and the valves were opened completely or partially. The light-band micrometer and the camera was started to record the droplet behavior. Afterwards, 20 μl of the solution was drop casted with a needle on the substrate. The cell was closed with the cap and, if necessary, the magnet was put on top of it. The time for closing the hutch, drop casting and starting of the measurement was between 3 and 5 minutes. The different parameters and the produced samples are listed in table 6.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Solution</th>
<th>Amount</th>
<th>Magnetic field</th>
<th>Reservoir</th>
<th>Valve</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^S_{Sh1.68,3.36}$</td>
<td>$S^8_8$</td>
<td>20 μl</td>
<td>$H_\perp$ 36 mT</td>
<td>no toluene</td>
<td>completely opened</td>
</tr>
<tr>
<td>$D^S_{Sh1.68,3.36}$</td>
<td>$S^8_4$</td>
<td>20 μl</td>
<td>$H_\perp$ 36 mT</td>
<td>100 μl</td>
<td>3 turns opened</td>
</tr>
<tr>
<td>$D^C_{Sh1.68,3.36}$</td>
<td>$S^8_8$</td>
<td>20 μl</td>
<td>$H_\perp$ 36 mT</td>
<td>no toluene</td>
<td>completely opened</td>
</tr>
<tr>
<td>$D^C_{Sh1.68,3.36}$</td>
<td>$S^8_4$</td>
<td>20 μl</td>
<td>$H_\perp$ 36 mT</td>
<td>100 μl</td>
<td>3 turns opened</td>
</tr>
<tr>
<td>$D^C_{Sh1.68,3.36}$</td>
<td>$S^8_8$</td>
<td>20 μl</td>
<td>no field</td>
<td>no toluene</td>
<td>completely opened</td>
</tr>
<tr>
<td>$D^C_{Sh1.68,3.36}$</td>
<td>$S^8_4$</td>
<td>20 μl</td>
<td>no field</td>
<td>no toluene</td>
<td>completely opened</td>
</tr>
</tbody>
</table>

Table 6.1: Sample parameters which were used for the ESRF in-situ experiment

104
6.3 Results and discussion

In this section we consider the time dependent behavior of a self-organizing system of spherical or cubic particles and compare them with measurements under different deposition conditions (see table 6.1). The determination of the position of the nucleation is a further challenge to solve.

6.3.1 Qualitative analysis of the data

After drop casting the particles onto a silicon substrate the droplet was measured repeatedly in transmission geometry at different heights above the silicon surface for the middle evaporation time and for the short one only at the lowest position to improve the time resolution. Grazing incidence measurements at 0.3° incident angle were started after the light-band micrometer displayed a value smaller than 50 µm. The acquisition time of 1 s and a readout time of 7 s defined our time resolution.

From the transmission experiments no sign of cluster formation in the fluid could be found. As can be seen in figure 6.4a as an example for a sample with spherical particles and short evaporation time, there is only a spherical form factor present at the beginning of the experiment (green), which does not show any significant change during evaporation until the droplet surface reaches the beam at its lowest position, where the total reflection makes further SAXS observation impossible (red area). An estimation for the possible measurable structure factor of clustered particles in a solution shows that \( \approx 5\% \) of all particles need to be bound in clusters to get a measurable signal (see figure 6.4b). A clustered paste of the same particles measured at

![Figure 6.4: Results from SAXS measurements](image-url)
an in-house lab source in SAXS geometry and normalized to the total scattering of the in-situ transmission measurement was used to get this estimation.

After in-situ SAXS measurements on the drying droplet, GISAXS images have been taken continuously until the experiment was finished. This geometry is mainly sensitive to the substrate but records clustering in the rest of the droplet film of a few µm as well. For the longer evaporation times the cover glass was removed after a given time when the nucleation was finished to speed up the final drying process. An excerpt of the GISAXS data taken for one experiment with a middle evaporation time for a spherical particle system is shown in figure 6.5. The insets show the (015) reflex magnified in a linear scale. The time evolution is nicely shown in these pictures. At the beginning, there is no sign of ordering, but the increasing intensity on the FF rings at the starting point of the nucleation shows an increasing of the density in the film of disordered nanoparticles. Suddenly, the self organization starts and sharp peaks with the beam profile develop (see figure 6.5c during nucleation). A closer look shows a shape with splitted peaks not mirror symmetrical around the Qz-axis, which clearly shows that this effect is not the result of the structure itself. As the size of the splitted parts at the beginning is even smaller than the measured instrumental resolution, this behavior can be explained by the drying front approaching the region covered by the beam footprint, so only a part of the 1mm beam is scattered, which improves the apparent resolution until the whole beam contributes to the peaks. Different peak regions are coming from different surface areas from the curved droplet front. Peaks sharper than the resolution result from a highly ordered system with nearly the same lattices constants in all areas and no tilting angle. The tilting angle describes the inclination between the mesocrystal c-axis and the substrate surface normal. The combined scattering of mesocrystals with different tilting angle leads to rotational broadening of all reflections up to the most extreme case of closed Debye-Scherrer rings for a 3D powder. This increased width, however, is no sign for a decreased structural coherence in each mesocrystal.
6.3 Results and discussion

For this evaporation rate, most of the ordering takes place within 9 minutes. In this time the amount of scattering centers grows, which causes the increase of the peak intensity (compare figure 6.5 during (c) to after nucleation (d)). During the nucleation time of the GISAXS pattern, we could observe an horizontal drying front with the microscope camera. The droplet is uniformly drying from the outer to the inner part. With the motion of this front more and more area of grown mesocrystals is accumulated, with a distribution of lattice constants and mesocrystal sizes indicated by the broadening of the peaks in $Q_z$ and $Q_y$ direction. During the nucleation the incoherent background reduced, due to the reduction of the number of free particles.

During the subsequent drying process (compare figure 6.5 after nucleation (d) to before opening (e)) the mesocrystal lattice parameters shrink, a distribution of lattice constants broadens and the crystals develop a random tilt around the surface normal, which leads to smeared reflections in tangential and radial direction around the position of the primary beam. The peak intensity decreases as no more mesocrystals are formed while the peak width gets larger. The opening of the cell due to time limitation of the beamtime induces a fast drying of the system and increases the tilting of the mesocrystals. While during the growth of the mesocrystals the lattice constants are similar, the drying of the grown crystals generates the tilting and different lattice constant. The measured GISAXS peaks are the result of a distribution of mesocrystals with different lattice constants and orientations.

After the experiments all samples exhibited order with the same known space group $R\overline{3}m$ for the spherical system and $I4/mmm$ for the cubic one. Although the degree of order (peak width) in the resulting assemblies vary with the given evaporation time the overall process was found to be similar for all samples. No structural transition is observed during the growth process. For a more quantitative analysis of the GISAXS pattern we developed a routine, which can fit the GISAXS peaks in dependence of the time. This procedure is described in the next chapter, where we analyze the drying properties in more detail.

6.3.2 Data evaluation

The time evolution of the ordering process was analyzed by fitting selected peaks for all recorded patterns. To obtain the correct peak shape a Fast Fourier Transform convolution of a beam shape function, a 2D Lorentzian function to model the mesocrystal correlation length ($\gamma_x$, $\gamma_z$) and a 2D Gaussian function with the radial $\sigma_r$ and tangential $\sigma_t$ standard deviations describing a random variation of the mesocrystal lattice parameters and tilting of the c-axis away from the substrate surface was used. The distorted-wave Born approximation was considered for the peak positions, a constant background, determined far away from the scattered intensity, was subtracted and the data was divided by the single particle form factor, leaving only the structure factor part of the scattering for better comparison and fitting of the peaks. More details about the fitting routine can be found in section 5.3.2.

For the spherical system as an example, 12 peaks were selected for fitting, (108), (104), (105), (113), (204), (116) and their mirror reflections with negative $Q_y$ values, as they exhibited enough intensity, don’t have too low $Q_z$ and are not very close to intense background regions. All peaks have been fitted together with coupled lattice constants (a, c), $\gamma$ and $\sigma$ parameters as well as $Q_z$ and $Q_y$ offsets to keep the number of free parameters as low as possible. The peak positions are no free parameter as they are defined by the reciprocal lattice. The intensities I are only coupled for each mirror pairs. The good agreement of the fit functions to the measured data
Figure 6.6: Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same $\sigma_r$, $\sigma_t$, $\gamma_x$ and $\gamma_y$ parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters.
6.3 Results and discussion

Figure 6.7: Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same \( \sigma_r, \sigma_t, \gamma_x \) and \( \gamma_y \) parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters.
Figure 6.8: Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same $\sigma_r$, $\sigma_t$, $\gamma_x$, and $\gamma_y$ parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters.
is exemplified in figure 6.6-6.8. The table A.1 in the appendix shows the fit results of theses three example pictures, the results of all fits for important parameters are shown in figure 6.10, figure 6.11a and figure 6.11b.

6.3.3 Four stages of the mesocrystal growth

The combination of the GISAXS fit results, the light-band micrometer data and the microscope images yield new details of the self-assembling and drying process. The resulting parameters are combined in table 6.2 and show the relationship between the used methods. The new insights will be explained on the next pages with the spherical samples. The cubic system behaves equivalent. In general the experiments can be divided into four stages (see figure 6.10):

Stage 1: After drop casting the solution on the silicon substrate, the surface is completely wetted, the droplet forms a meniscus (see figure 6.9a) and is slowly shrinking in height. The decreasing height of the droplet is recorded by the light-band micrometer (green), which shows that during this first stage almost the full height of the droplet vanishes. Only a few µm are left at the end of the first part. The wetting angle gets smaller and a thin film of nanoparticle solution is generated. It is possible to perform SAXS measurements only in this stage as long as the beam is smaller than the residual droplet height. The incoherent form factor, which indicates the density of disordered particles, shows only a slower increase for the middle evaporation time and a faster one for the short experiment. No sign of ordering could be observed. This phase is observed in all measurements, equally for different evaporation times. The main difference observed is the time the samples stays in this stage. A short evaporation needs only a few minutes, in contrast to long evaporation times where the droplet stays hours in the saturated atmosphere. This stage is referred to as vertical droplet reduction.

Stage 2: In the next stage, so called highly concentrated film, a flat film of highly concentrated colloidal solution is observed as constant in the camera (figure 6.9b), while the LBM shows a small decay to zero (or a constant offset). The integrated intensity of the incoherent background shows a nonlinear increase of the density of the nanoparticle solution (figure 6.10). The meniscus collapses and the evaporation of the toluene is ongoing. This behavior is only observed in the medium and long evaporation times, at which the saturated atmosphere inhibits

<table>
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<tr>
<th>Sample ID</th>
<th>1st stage</th>
<th>2nd stage</th>
<th>3rd stage</th>
<th>Duration$_{zero}$</th>
<th>height$_{start}$</th>
<th>speed</th>
<th>GISAXS Duration$_{nuc}$</th>
</tr>
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<tr>
<td>D$_{S, 5.01 \times 36}$</td>
<td>6-7 min</td>
<td>/</td>
<td>3-4 min</td>
<td>6-7 min</td>
<td>245 µm</td>
<td>-0.604 µm/s</td>
<td>2.5 min</td>
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<td>D$_{S, 5.01 \times 36}$</td>
<td>38 min</td>
<td>26 min</td>
<td>11 min</td>
<td>44 min</td>
<td>300 µm</td>
<td>-0.066 µm/s</td>
<td>9 min</td>
</tr>
<tr>
<td>D$_{C, 10.9, 0.8 \times 36}$</td>
<td>7 min</td>
<td>/</td>
<td>4 min</td>
<td>9 min</td>
<td>315 µm</td>
<td>-0.580 µm/s</td>
<td>4 min</td>
</tr>
<tr>
<td>D$_{C, 10.9, 0.8 \times 36}$</td>
<td>41 min</td>
<td>35 min</td>
<td>10 min</td>
<td>77 min</td>
<td>335 µm</td>
<td>-0.073 µm/s</td>
<td>7 min</td>
</tr>
<tr>
<td>D$_{S, 5.01 \times 36}$</td>
<td>11 min</td>
<td>/</td>
<td>3-4 min</td>
<td>12 min</td>
<td>400 µm</td>
<td>-0.58 µm/s</td>
<td>2 min</td>
</tr>
</tbody>
</table>

Table 6.2: Received values from the LBM, camera and 3D GISAXS pattern. Duration$_{zero}$ shows the time until the LBM value is zero. Duration$_{nuc}$ is the value for the nucleation, which is read out the 3D GISAXS pattern. The errors for the time values read out from the camera is 0.5 min, for the LBM 0.1 min and from the GISAXS pattern 0.5 min.
Figure 6.9: Sketch of the four stages of the droplet drying. The insets show the corresponding pictures of the microscope camera, which are in good agreement.
too fast evaporation. In GISAXS, no sign of order is found in this stage. Obviously a critical concentration is needed for the nucleation of the 3D systems.

**Stage 3:** The next period, which is called horizontal drying front or nucleation, is recorded with the camera for every sample. A circular inward movement of the contact line\(^1\) is observed (figure 6.9c and figure 6.9d). When the drying front approaches the beam footprint and the necessary concentration is reached, a sudden nucleation starts and sharp peaks from the mesocrystal order appear. The peaks get stronger as more and more mesocrystals form in the area illuminated by the x-ray beam. This phenomenon is directly measurable by the integrated intensity of the peaks from the fitting routine (figure 6.10). Simultaneously the amount of disordered particles decreases as is indicated by a rapid decay of incoherent scattering intensity. The time between the start and the end of the nucleation (the main mesocrystal growth) is approximately 3 minutes for the short measurement and 9 minutes for the long ones. This time frame corresponds to the time the pinning line needs to move from the outer to the inner part and the droplet is fully dried. As the beam footprint ranges from the sample center to about 2/3 of the sample surface, the contact line is only observed a bit later. Thus the measured nucleation period from GISAXS is often shorter compared to the microscope. This effect is an indication that the self-organization happens at the drying front of the droplet in the 3rd stage. The position of the nucleation and the growth process is therefore identified as the substrate-liquid-air interface (so called triple phase contact line TPCL [76]).

The peak shape does not change significantly during this first growth step (see figure 6.11a). The jump at the beginning is a numeric artefact, as the radial \(\sigma\) part has no influence when it is much smaller than the intrinsic beam width. During the nucleation, mesocrystals with a low lattice constant deviation and tilting exist. The behavior of \(c\) and \(a\) shows a quick decay in the nucleation stage (figure 6.11b), which slows down afterwards. This effect shows the nonlinear behavior in this part, it is much less pronounced for the longer evaporation times, because we average over a lot more different drying times of the mesocrystal growth in contrast to the short experiments.

A better degree of order can be observed for the medium evaporation time sample, because the particles have more time to order during the nucleation stage (see section 4.2.4.3), as well for the first and the additionally second stage.

**Stage 4:** The last stage is the drying stage, where no significant mesocrystal formation is taking place. This is easily seen in figure 6.10, where the integrated intensity stays constant. No new scattering centers appear inside the observation area. The mesocrystals are drying and the toluene between the ordered particles evaporates, so that the distance between the individual nanoparticles decreases. This leads to a movement of the peaks towards higher \(Q\) values, which is shown in figure 6.11b. The extracted lattice constants \(c\) and \(a\) contract simultaneously and the ratio between \(c\) and \(a\) drifts as well, showing that the shrinking is neither isotropic nor in a single direction. Comparing the \(c/a\) value with 2.45 expected for a perfectly closed packed structure shows, that the unit cell is extended in \(c\) direction when nucleated, approaching the fcc packing and even slightly compressing at the end of the short experiments. In all cases the observation time was not long enough to reach a stable state, so the finally approached values can only be guessed to be close to the perfect fcc structure. The starting and end values of the relation are higher for the longer evaporation time.

---

\(^1\) The connection between the substrate and the end of the droplet.
Chapter 6 Time evolution of mesocrystal growth

Figure 6.10: Integrated intensity of the peak and incoherent background versus time in comparison to the height of the droplet measured by the LBM. The four stages of the mesocrystal growth independently observed with the LBM are indicated by the colored regions for the measurement with medium evaporation time (pale colors) and by the gray lines for the short evaporation time (strong colors). The value \( t_0 \) describes the starting time of the nucleation. Each intensity point is the result of the GISAXS data treatment of one measurement described in section 5.3.2.

Figure 6.11: Comparison of structural parameters versus time. Due to necessary available ordered system for this investigation, only the last two stages are indicated by the colored rectangular in the background for the medium measurement (pale colors) and by the gray lines for the short evaporation time (strong colors). The value \( t_0 \) describes the starting time of the nucleation. The black line indicates a perfect closed packed lattice, which will be crossed for every sample.
In addition to the integrated intensities, the fit yields structural quality parameters, which are shown in figure 6.11a. Both sigmas have the same qualitative behavior, they increase with time, so the peaks get broader. The tilting of the mesocrystal, as well as the distribution of the lattice constants increase with the longer drying time. For shorter evaporation time and less toluene reservoir both effects are stronger. At least the evaporation of solvent in the center of the mesocrystal during the final drying stage will lead to the large observed spread of lattice constants, so that the observed GISAXS peaks are an integration over mesocrystals with different lattice constants. In the average a tilting angle of $3^\circ$ for the longer and $5^\circ$ for the short evaporation time is observed.

6.4 Conclusions

An in-situ GISAXS study of highly ordered nanoparticle assemblies was carried out, to get a deeper understanding of the self-assembling process of the 3D system. A specialized in-situ cell was build to measure the crystal growth of nanoparticles in real time. Simultaneous measurements of high spatial resolution GISAXS, light band micrometer and microscope measurements could yield a new insight in the droplet evaporation and nanoparticle ordering. Precise control of the system and accurate identification of key features was possible. The highly ordered system, as well as a new fit function enabled new observations and a more quantitative understanding of the process.

In general the evaporation induced mesocrystal growth could be divided into four stages:

- **Stage 1 - vertical droplet reduction**: The droplet is cast on the silicon, forms a meniscus and slowly evaporates in the experiment with strongly saturated atmosphere, while a faster decay is observed for the short measurements. No sign of order can be found in this stage. The incoherent form factor, which indicates the density of disordered particles, shows only a slower increase for the middle evaporation time and a faster one for the short experiment.

- **Stage 2 - highly concentrated film**: The meniscus collapses and a constant, highly concentrated flat film is visible. No sign of ordering is found in this stage as well. The incoherent background shows a nonlinear increase of the density of the nanoparticle solution, which indicates that the evaporation of the toluene is ongoing. This stage is only observed for the samples with longer evaporation time.

- **Stage 3 - nucleation**: Suddenly, the contact line of the droplet moves circularly inward, the nucleation starts and sharp peaks from the mesocrystal order appear in the GISAXS pattern. Peaks get stronger as more and more mesocrystals form in the area illuminated by the x-ray beam. The nucleation period is longer for longer evaporation time.

- **Stage 4 - drying stage**: In the last stage no significant new mesocrystal formation is taking place. The mesocrystals are drying and the toluene between the ordered particles evaporates, so that the distance between the individual nanoparticles decreases.

The position of the nucleation and the growth process is identified as the substrate-liquid-air interface (so called triple phase contact line TPCL). While previous publications stated that the
evaporation kinetics and the amount of excess dodecanethiol ligand molecules affected monolayer formation at the liquid–air interface [22, 65], the iron oxide particles by Roth and Siffalovic et.al. [76, 82, 83] formed a monolayer at the TPCL. In this case the monolayer formation is similar to the 3D growth of spherical nanoparticles. SAXS measurements at different heights of the drop volume during evaporation show neither cluster formation at the drop surface, nor nucleation in the drop volume until a droplet height of a few µm. This result supports a process as described by Siffalovic et.al. [83] for the mesocrystal formation at the TPCL. The concurring explanation in [28] does not hold in our case as it should be possible to measure a monolayer formation inside the drying droplet at the liquid–air interface. The agreement of the time between the start and the end of the nucleation observed by GISAXS and the time the pinning line needs to move from the outer to the inner part is a further indication.

A critical concentration is necessary to start the mesocrystal growth, so the nucleation starts when the drying front of the droplet moves over a given position on the sample. Gonuguntla et.al. [47] report an existing increased evaporation near the contact line, which leads to an advection current that transports material in the drop toward the periphery. The high concentration, as well as the possible interaction with the substrate create ideal conditions for mesocrystal growth at the contact line. When the front reaches the illuminated area, the formation happens very quickly, so that the first visible peaks are already very narrow. As a consequence the only dynamic process observable in our experiment is the aggregation of more mesocrystals creating a statistical distribution on the sample surface and the much slower drying of already formed mesocrystals, changing their lattice parameters.

Unfortunately the nucleation process is not visible due to the limited time resolution in the order of seconds, disordering of the perhaps existing clusters or the low signal of these precursors. We can rule out a coherent nucleation process over the whole sample area, as small clusters formed by at least 5% of the particles inside the solution would have been visible as was shown by comparison to the SAXS measurement on particles clustering in solution.

Our main focus was to observe the influence of different evaporation times on the growth mechanism. A higher evaporation time allows the sample to stay longer in each stage, additionally a second stage is observed. A better degree of order can be found, as well, because the particles have more time to order in the final nucleation stage. Although the time particles spend in the free solution seems to have no influence for the self organization, the slower evaporation leads to a decreased movement of the TPCL, where the ordering is supposed to take place. As the movement of the TPCL is slower, more time is available during the final nucleation stage, allowing a better degree of order, too. In addition, the reduced drying rate can lead to a reduction of crack formation and similar effects, that reduce the structural quality of mesocrystals after the growth is finished. Furthermore it can be explained by a larger diffusion radius for the particles allowed by the slower evaporation, which can lead to accumulation of particles with similar size and shape, allowing better long range order. This theory is supported by the observation of self separation of cubic and spherical particles in a mixed solution as described in chapter 4.

The time dependent fit of multiple peaks yielded additional quantitative information about the drying of the mesocrystal. While the mesocrystal is shrinking the lattice constants c and a contract simultaneously and the ratio between c and a drifts as well, showing that the shrinking is neither isotropic nor in a single direction. Comparing the c/a value with 2.45 expected for a perfect closed packed structure shows that the unit cell in c direction is extended when nucleated, approaching the fcc packing and even slightly compressing at the end of the short experiments.
In all cases the observation time was not long enough to reach a stable state, so the finally approached values can only be guessed to be close to the perfect fcc structure. It was found that the starting and end values of these lattice constants are higher for the longer evaporation time. This could be explained by the fact that particles with a bigger radius have a slower movement inside the solution and could order in a mesocrystal only when given enough time. A too short evaporation time avoid the growth of mesocrystals with bigger particle, which leads to lower averaged lattice constant values. Although the degree of order (peak width) in the resulting assemblies varies with the given evaporation time, the overall process was found to be similar for all samples.

In summary, a deep insight into the 3D self-assembly process for spherical particles was obtained. Unfortunately, some aspects could not be clarified conclusively with the performed experiment. For example the measurement of the nucleation stage would profit from a much higher time resolution and smaller beam size.
Chapter 7

Diffraction from a single mesocrystal

Another aspect of this PhD work is to understand the exact 3D structure of one single mesocrystal formed from magnetic nanoparticles using the already established deposition methods. The basis of this study was a completely new approach: Performing a diffraction experiment on a single, isolated mesocrystal with a micro-focus x-ray beam. This experiment makes it possible to measure the mesocrystal peaks without the in-plane orientational average and without background from disordered regions. In previous GISAXS experiments, the peak shape has been broadened due to the average over the ensemble of mesocrystals with a statistical variation of lattice constants or tilting angle to the substrate (chapter 5). These effects are not present when considering only a single mesocrystal.

Separation of a single mesocrystal of nanoparticles from an ensemble of mesocrystals as-grown is a completely novel process as well. This experiment is not only interesting from a scientific point of view, but enters a new level of crystallography. Diffraction experiments to investigate the atomic structure of solids and crystals in the Å-range is a well established method [39, 57, 78, 79]. Larger building blocks of crystals in the nm-range were studied on self-assembled crystals of fullerenes [62, 97] or proteins [56, 77] already. In this work we increased the challenge by performing diffraction experiments on 3D self assembled nanoparticle crystals with building blocks in the 10 nm -range and forming small crystals of a few 100 nm height with a sample volume in the range of 1 µm³. So far small crystals investigated for the atomic structure are reported with a volume in the 100 µm³ range [16, 17, 48]. In contrast to the former crystals built of large molecules, the nanoparticle building blocks are not exactly equal in their atomic structure and surrounded by a soft organic shell. Therefore the resulting crystalline order is slightly different.

7.1 Separation of a single mesocrystal

For the single mesocrystal preparation one crystal is isolated from a standard sample with an ensemble of mesocrystals using Focused Ion Beam preparation (FIB). The 2D powder samples were produced with the best parameters known to achieve a well ordered structure, which was investigated for this kind of samples by GISAXS analysis (see section 4.2.4). The FIB preparation was done with a FEI Dual Beam System Helios NanoLab 400S. A dual beam system combines the advantage of a scanning electron microscope (SEM) and a focused ion beam instrument. In the SEM, secondary electrons (SE) are generated through the low-mass electrons interacting with the sample surface non-destructively. Collected SE offer an image resolution
Chapter 7 Diffraction from a single mesocrystal

(a) Searching for a free standing and good ordered mesocrystal.
(b) Covering a mesocrystal with a Pt layer.
(c) Cutting of the two trenches.
(d) Transferring the block to a copper Omniprobe® grid
(e) Fixing the block with platinum.
(f) Clearance cutting of a mesocrystal.

Figure 7.1: Description of the extraction process of a single mesocrystal (highlighted in color).

Figure 7.2: Single mesocrystal sample as used.
7.1 Separation of a single mesocrystal

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2D powder sample ID</th>
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<th>height</th>
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<td>3.45± 0.1 µm</td>
<td>361± 80 nm</td>
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<tr>
<td>M₂S</td>
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<td>R3m</td>
<td>2.45± 0.1 µm</td>
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<td>I4/mmm</td>
<td>4.50± 0.1 µm</td>
<td>215± 80 nm</td>
</tr>
</tbody>
</table>

Table 7.1: Produced mesocrystals which were used for the diffraction experiment and their main parameters.

down to sub-nanometer range. The FIB is similar to a SEM, but utilizes a beam of higher-mass Gallium ions, which induce a sputtering process that modifies the surface with nanometer precision. In this Dual Beam system the electron and the ion beams intersect at a 52° angle at a coincident point near the sample surface. This allows in-situ SEM imaging of the FIB milling process and allows one to precisely cut out a single mesocrystal from the 2D powder sample. The information about the FIB system presented here was taken from the manufacturers website [105]. The separation process was done in collaboration with Doris Meertens from the Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons. In this chapter a detailed description of the separation process is given and illustrated with some example images.

At the beginning a mesocrystal, which is well separated from others and shows a nice structure on top (figure 7.1a) has to be found with SEM. On top of the chosen mesocrystal a Pt-layer of 300-500 nm is deposited with an electron beam of 5 kV and 5.5 nA, exemplified in figure 7.1b. This Pt-layer protects the mesocrystal from the focused ion beam, which will be used for the detaching process of the chosen mesocrystal from the substrate. During the carving process the neighboring mesocrystals are destroyed by the high energetic ions.

For the extraction of a mesocrystal with an underlying Si block as bottom support, two trenches around the chosen crystal have to be cleaved with an ion beam of 30 kV and 6.5 nA using the parameter for milling Silicon (see figure 7.1c). Thereafter, one side block and the bottom area are cut free. The substrate block with the mesocrystal on top has to be large enough to allow the fixation with platinum at the tungsten manipulator needle with enough distance to the mesocrystal. The second side block is removed and the pieces with the mesocrystal hangs freely on the tip of the tungsten needle.

The block is transferred to a copper Omniprobe® grid, which is a standard holder for mounting TEM lamellas milled out by FIB systems (figure 7.2b) and attached to the top of the middle grid position B, trying to keep the c axis orientation upwards (figure 7.1d, figure 7.2c). The block is fixed with platinum (ion beam 30 kV and 93 pA) to the Omnipgrid® (see the stripes of Pt at the backside in figure 7.1e). Then the manipulator needle is detached from the specimen and the final preparation of the single mesocrystal can be started. Layer by layer everything around the single mesocrystal is dissipated (figure 7.1f). From the outside to the inside, one ring after the other is excavated with an ion beam of 30 kV and 93 pA. Slowly getting closer to the core of the mesocrystal, while constantly taking SEM images to control the process. Undesirable edges of the silicon around are removed to have a free path for the x-ray beam through the mesocrystal. The platinum protection layer on top has to persist to avoid damaging the mesocrystal. Finally a fully isolated mesocrystal is achieved (figure 7.2d), which is well oriented upwards with the [001] direction of the silicon substrate. This known orientation of the mesocrystal helps with the alignment for the scattering experiment. The crystalline order of the mesocrystal is
not destroyed by the procedure as indicated in figure 7.2e. For the diffraction measurement the copper grid was fixed on a row bar holder figure 7.2a, which could be transported in a special box and could be inserted into a dedicated sample holder at the beamline. The produced single isolated mesocrystals, that were subsequently investigated by x-ray diffraction, are listed in table 7.1.

7.2 Experimental details

To be able to investigate crystals of $\mu$m size some requirements are absolutely mandatory: The x-rays have to be focused down approximately to the size of the crystal to achieve high photon flux densities, the beam has to stable within a fraction of the beam diameter, the background has to be virtually zero and the motor resolution has to be significantly better than the sample size. These necessary conditions make this experiment an absolute challenge. The investigation was done with a focus spot size of 5 $\mu$m vertically and 10 $\mu$m horizontally to measure crystals with $\approx$300 nm height and a few $\mu$m width. The samples have a small scattering volume and thus provide weak intensities, so a focusing down to close to the sample size is required to increase the signal and even lower the background. This small spot size induces other challenges as to find the sample in the first place with such a small beam. For each crystal orientation the xyz-position needed to be realigned to bring the mesocrystal into the beam center as the sphere of confusion of the six-circle was in the order of the beam size. For a measurement with lower focusing (see M$^I_2$, which is the only sample measured with 50 $\mu$m vertically and 200 $\mu$m horizontally) more background from other regions around the sample and low peak intensities are visible. So the decision was clear to use the fully focused beam, although three days of sample alignment were necessary.

The diffraction experiment was performed at the high resolution diffractometer P08 at Petra III (figure 7.3, see section 3.8 for the instrumental details). After alignment of the beamline and the exact determination of the beam position, the single mesocrystal was fixed on a special setup on the sample holder (figure 7.2a) and aligned optically with a microscope camera to the beam position. The copper grid B was clearly visible and could easily be aligned. The crystal itself was not optically visible, but could be guessed from a blue spot, which was produced by the Si block under the crystal by reflections from the illuminated silicon. For the rough positioning of the sample on grid part B, we used a NaJ point detector measuring the beam attenuation due to the Cu sample holder (attenuation due to the small mesocrystal or silicon substrate was too weak to be detected with a beamsize of 10 $\mu$m horizontally and 5 $\mu$m vertically). The next step was to find a Si peak and to carry out a precise adjustment of the goniometer angles with the Si (004) reflection to align Si (001) and thus the mesocrystal (001) direction parallel to the axis of the phi motor. This way the orientation could be found very precise to a few hundredths of a degree, in contrast to about 0.5 $^\circ$ when using the mesocrystal structure reflections. With this orientation the phi motor could be used to rotate the sample around its (001) direction. To locate the small silicon substrate (5x10x10 $\mu$m$^3$) and its Si(004) reflection, the Roper Scientific detector was used. The detector has a high resolution and is optimized for the used energy of 12.4 keV. The same detector was used to search for the mesocrystal reflections, afterwards. After discovering the nanoparticle superstructure peaks, a fine adjustment was done to maximize the reflex intensities.
7.2 Experimental details

For the scattering pattern measurements, different reciprocal lattice planes were selected by rotating the crystal around the \( \phi \)-axis, optimized in the position and measured by rocking the crystal in both \( \omega \) and \( \phi \). In detail, images were exposed while continuously moving \( \phi \) for 5 separate \( \omega \) positions ("cmesh"). A sketch of this cmesh procedure is shown in figure 7.4. The scans were measured for \( \phi \) in the range of \( \pm 3.5^\circ \) and for \( \omega \) in the range of \( \pm 1^\circ \) around the position where the left and the right as well as the bottom and top equivalent reflexes have about the same intensity on the detector. With the used wavelength all mesocrystal reflections with reasonable intensity have small diffraction angles < 3^\circ and thus the Ewald sphere is very flat and several reflections can be observed simultaneously (as in the GISAXS case section 4.2.3). However, the high resolution of the synchrotron beam, which corresponds to a narrow "shell" of the Ewald sphere, inhibits the simultaneous observation of the full scattering plane and reflections at higher \( Q \) appear much weaker, as they are further away from the perfect diffraction condition (Bragg condition). The optimal measurement range for \( \omega \) and \( \phi \) would reach from the Bragg angle of the lowest \( Q \) reflection to the highest \( Q \) reflection, which is about \( 1.5^\circ \) for the (004) reflection, which is still visible on the observed detector range. In our experiment the cmesh areas where chosen as as given above, so for the \( Q_y \) direction this optimal conditions are fully satisfied while the \( Q_z \) is a compromise between measurement time and covered area/step size. As the \( \phi \) direction is scanned during exposure, it is possible to make very small steps over a large area without increasing the counting time (in our case 60 s for 70 steps) as the detector does not need to be read out between each step. \( \omega \), on the other hand, needs to be done in discrete steps and thus each additional step increases the counting time. As can be seen in the measured figures, this selected area is sufficient to access all peaks in the detector area. For comparing the images with simulated intensities, these experimental conditions needs to be considered as well, as they lead to e.g. lower observed intensities for all reflections with the Miller indices \( l>3 \).

To obtain integrated intensities of the reflections necessary for a quantitative structure analysis
of a single mesocrystal, rocking scans of peaks of the cubic system for all accessed planes were performed. To achieve a well defined and optimized rocking scan of a reflection, the mesocrystal was aligned using the chi angle to bring the reflections in vertical direction. This way the omega angle could be used to scan the peaks perpendicular to their \( \vec{Q} \) direction, thus the \( \omega \)-scan is equivalent to a scan in \( \vec{Q}_x \) direction. As the sphere of confusion of the six-circle was of the order of the beam size, it was necessary to realign the xyz-position for each \( \chi \) orientation to bring the mesocrystal into the beam center.

A first attempt of wide-angle diffraction was tried for the (220) peak at 19.5° detector angle. The goal was to search for a preferred crystalline orientation of the nanoparticles inside one mesocrystal. Low intensity peaks were expected, but we could not detect anything within reasonable counting times. Additionally, we had to avoid a region of reciprocal space around a Bragg reflection from Cu. A later estimation based on the intensity ratio between the mesocrystal and \( \gamma \)-Fe2O3 (004) reflexes of \( 3 \times 10^{-4} \) measured on the laboratory reflectometer with a \( \theta2\theta \)-scan for a 2D powder sample resulted in an expected peak intensity of \( 1 \times 10^{-3} \) c/s for the MC. This intensity would have been impossible to measure given our experimental conditions with an average background of 1-2 c/s.

### 7.3 Result and discussion

In this challenging experiment we succeeded to measure three single mesocrystals, two with spherical and one with cubic particles (see table 7.1). This section is split in two subsections. The first one shows a selection of different reciprocal lattices and a discussion about the crystal structure and their quality. In the second part an integrated Intensity analysis is done for the cubic sample to give a quantitative approach to the structure analysis. The description of the nomenclature used for the angles is given in section 3.8.

#### 7.3.1 Analysis of the scattering pattern

Different reciprocal lattice planes were measured by rocking the crystal in both \( \omega \) and \( \phi \). For each of the five recorded pictures at different \( \omega \) positions a measurement period of 60 s and one additional background measurement with equal time was chosen. One c-mesh including background measurement needs more than 10 min and is repeated a number of times in dependence of the expected scattering intensity. Such a measurement was done for all selected planes. For the data treatment the different scans for \( \omega \) are combined using the maximal pixel intensity of each individual image. This procedure is advantageous compared to summing up all images as it reduces the relative background (BG). The average BG for all images is comparable while the peak is only present in some images. Thus the BG sum is \( \approx 5 \cdot \text{BG}_{\text{max}} \) while the peak sum is \( \approx (1 - 2) \cdot \text{peak}_{\text{max}} \). The repeated cmesh’s are combined by averaging. A selection of pictures, which were recorded from different planes, is represented in components of the scattering vector and reciprocal lattice units in figure 7.6 and figure 7.7. For an complete overview, all images left out in this section are shown in appendix table A.2 of the appendix. To prevent confusion of the parameter symbols retrieved from fits of the single mesocrystal data with the ensemble parameters the former are marked with MC subscript, which abbreviates single Meso.
Crystal. MC is in a sense relate to the previous use in the form factor formulas in chapter 5 as both symbols describe physical parameters of only one mesocrystal.

The non-uniform background scattering, spreading "beam like" from the center, is different but present in every scattering plane. It looks like a shadowing effect from something inside the beam path. Equivalent reflexes of for example (301) and (30T) of the (h0l) plane from the $M_{C}^\prime$ have not the same intensity. While the (301) reflex has a similar intensity as the other reflexes which are lying on the same $|Q|$ of the form factor ring, the (30T) is obviously weaker and lies on a shadowed cone. Due to the impact on the reflexes, it is possible to assume that the object or the reason for the shadowing effect is positioned behind the sample. Shadowing of silica pillars, which are a residue from the separation process of a single mesocrystal, can be excluded, because the beam path seems to be open (see figure 7.5). The reason could be situated inside the flight tube behind the sample. A low $\phi$ dependence of the non-uniform background supports this possibility, as the tube is fixed. Additionally a halo effect from the residual direct beam is visible. The absorption by the silicon substrate of the scattered beam creates a reduced BG in the lower hemisphere.

7.3.1.1 Structure

Reflections for four independent reciprocal lattice planes for $M_{C}^\prime$ (figure 7.6a (h0l), 7.6b (hhl), A.13a (h2hl), A.13b (h3hl)) , three for $M_{S}^\prime$ (figure 7.7a (h0l), 7.7b (hhl), A.12b (0kl) ) and one for $M_{II}^\prime$ (figure 7.8 (hol)) have been detected.

For the mesocrystal with cubic building blocks we found: Repetitions as a function of $\phi$ of selected planes have been verified, proving a fourfold rotation axis parallel to $c_{MC}$ for the cubes crystal and together with $a_{MC} \neq c_{MC}$ (see table 7.2) and the identical 90°rotated crystal planes (hhl) and (hhl) the mesocrystal system is confirmed to be tetragonal. For the tetragonal system the zonal selection rules are:

(h0l) $h+l=2n$ (tetragonal ⇒ (0kl) $k+l=2n$)

(hhl) $l=2n$

(h2hl) $h+l=2n$ (tetragonal ⇒ (2hhl) $h+l=2n$)

(h3hl) $l=2n$ (tetragonal ⇒ (3hhl) $l=2n$)

Combining all these planes leads to the general selection rule $h+k+l=2n$ with no additional selection rules. Note that reflections extinguished by the form factor have not been taken into account, as e.g. (103), which is the main difference to crystal diffraction where the FF generally leads to no extinctions. This selection rule refines the system to a I-centered tetragonal lattice with one of the following space groups: I4, I4/m, I4mm, I4m2, I4/mmm, I422, I42m and I4. We expect to have the one with highest symmetry, I4/mmm, due to our simple unit cell containing only two particles (particle volume inhibits any higher number for this unit cell size). In addition to the selection rules there are three independent mirror planes visible, which in deed allow the refinement of the symmetry to I4/mmm. The (h0l) as well as the (0hl) plane...
Chapter 7 Diffraction from a single mesocrystal

Figure 7.6: Diffraction pattern from a single mesocrystal with cubic building blocks for different reciprocal planes. A simulation of these patterns is shown in the appendix section A.3.3.
7.3 Result and discussion

(a) Spheres $M_S^I$: measurement of the (h0l) plane

(b) Spheres $M_S^L$: measurement of the (hhl) plane

Figure 7.7: Diffraction pattern from a single mesocrystal with spherical building blocks for different reciprocal lattice planes.
show 2 mirror planes and due to the planes are perpendicular to each other the 3 mirror planes are necessary.

The crystal with spherical building blocks shows a three fold symmetry of the lattice from the repetitions as a function of $\varphi$ of selected planes. The observed reflections clearly follow $-h+k+l=3n$ with no additional selection rules. This selection rule refines the system to a R-centered lattice with one of the following space groups: R32, R3, R3m, R3 and R3m. We expect to have the one with highest symmetry, R3m, due to our simple unit cell containing only three particles (particle volume inhibits any higher number for this unit cell size).

In contrast to an atomic crystal (when ignoring orbital arrangement as typically done in diffraction), the symmetry of the individual building blocks needs to be considered for the space group determination, as well. All symmetry elements from the mesocrystal unit cell have to be applied to the single particle form to test this. For spherical particles this is trivial, as all symmetries will be present, when they are positioned at their center. For a cube (as well as for a truncated and rounded cube) the fourfold symmetry axes through the face centers, the three mirror planes and the inversion symmetry are all present, when it is aligned parallel to the unit cell (the same orientation as the unit cell). Different particle orientations (like placing the cube with the edge or corner upwards) would violate at least one fourfold axis or mirror plane.

$M^I_C$ and $M^I_S$ show a single crystalline structure, in contrast $M^II_S$ has a twinned structure with multiple grains. The observation of both reflections e.g. (101) and (011) shows the presence of 180° twinning, either resulting in peaks following $-h+k+l=3n$ or $h-k+l=3n$. This twinning structure is verified independently for these samples by TEM, made from a mesocrystal of the same sample (figure 7.8). Different colors inside the TEM as well as in the GISAXS picture indicate each twin orientation. The similar peak shapes of (011) and (011), arising from the same twin, are consistent with this. The observed rhombohedral R3m structure, which is the standard setting, as well as the reversed rhombohedral structure, where the $a_{MC}$ and $b_{MC}$ axis are rotated by 60° around $c_{MC}$, is another way of describing the twin relation. Reflexes on the (00l) line are coincident for both crystal orientations.

The indexed peaks of a single mesocrystal are consistent with the suggested R3m symmetry for spheres and I4/mmm space group for crystals made of cubes derived for an ensemble of mesocrystals. While the analysis of the GISAXS pattern deliver an average structure of all mesocrystals, in this experiment the structure of one crystal is determined uniquely.

### 7.3.1.2 Lattice constant and correlation length

The lattice constants and correlation lengths determined as an average over peaks of different planes in reciprocal space from every sample are shown in table 7.2. The individual values of the reflections are listed in appendix table A.2, where the parameters from two mirrored peaks ((hkl) and (hkl)) were averaged to compensate potential shifts due to an imperfect zero position of the detector. In table 7.2 the average is taken over all accessible peaks from the table in the appendix for each mesocrystal. To define the positions and half widths of the reflexes, a Gaussian fit was used. The parameters of $M^II_S$ are taken directly from the picture, as the peaks were not fittable. The extraction of intensity along the horizontal and vertical detector directions corresponds to coupled Qy (horizontal) or Qz (vertical) and Qx scans, however the Qx variation is negligible in our scattering geometry (small angles at the used wavelength) and furthermore
### Result and discussion

#### Sample ID

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\langle a_{MC} \rangle$</th>
<th>$\langle c_{MC} \rangle$</th>
<th>$\langle \varepsilon_{yMC} \rangle$</th>
<th>$\langle \varepsilon_{zMC} \rangle$</th>
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</thead>
<tbody>
<tr>
<td>$M_{II}^c$</td>
<td>11.86 ± 0.15 nm</td>
<td>21.04 ± 0.7 nm</td>
<td>362 ± 163 nm</td>
<td>244 ± 136 nm</td>
</tr>
<tr>
<td>$M_{II}^s$</td>
<td>11.62 ± 0.2 nm</td>
<td>24.62 ± 0.4 nm</td>
<td>1.1 ± 0.55 μm</td>
<td>172 ± 86 nm</td>
</tr>
<tr>
<td>$M_{I}^c$</td>
<td>12.17 ± 0.2 nm</td>
<td>25.44 ± 0.4 nm</td>
<td>741 ± 371 nm</td>
<td>167 ± 84 nm</td>
</tr>
<tr>
<td>$M_{I}^s$</td>
<td>12.28 ± 0.2 nm</td>
<td>19.98 ± 0.4 nm</td>
<td>782 ± 391 nm</td>
<td>207 ± 104 nm</td>
</tr>
<tr>
<td>$M_{II}^c$</td>
<td>13.47 ± 0.03 nm</td>
<td>15.08 ± 0.07 nm</td>
<td>923 ± 350 nm</td>
<td>309 ± 93 nm</td>
</tr>
</tbody>
</table>

#### Table 7.2: Lattice constant and correlations length from the average of reflexes from different planes of the single mesocrystal measurements. For $M_{II}^c$ the (h0l) plane was used. Due to asymmetric peak shapes and unknown factors as e.g. influence of the measurement method on the peak shape, the width are expected to be increased. The different colors red and cyan belong each to one twin according to figure 7.8. The three grains with the same orientation, enumerated in the scattering image figure figure 7.8, have been treated separately to derive the data shown and are color coded here as 1, 2 and 3. For a comparison the lattice constant values for an average over an ensemble of mesocrystals are shown below the line.

A reduced $\langle c_{MC} \rangle$ lattice constant of about 37% for cubic and 33% for spherical particles is observed for the investigated single mesocrystals in comparison to the averaged values from GISAXS results of a 2D powder sample (see results in section 4.2.4.1) produced under the same conditions and from the same particle solution. The average in-plane lattice constants from all observed reciprocal lattice planes shows only a slightly reduced value of about 5% for the cubic and 7% for the spherical nanoparticles. The lattice constants depend on the sample age, providing the drying time. Gradual evaporation of rest toluene between the particles inside a mesocrystal can reduce the distance between the particles and the reflections move to higher Q values. Additionally the in-situ experiments show that a constant value of the c/a axes is not reached after a day and it can be assumed that the drying of crystals needs a long time. The smaller lattice constant in comparison to the ensemble of mesocrystals could be caused by the fact that the 2D powder sample is being dried in a vacuum system a few days before detaching the single mesocrystal. Furthermore the separated mesocrystal is free standing which could lead to an increased drying rate. Additional influences of the Pt cover layer as well as the selection of a mesocrystal formed from slightly smaller particles than the average is possible, as well. After section 4.2.3 it is expected that similar particles will order together in one mesocrystal, so it is not surprising that the large crystals selected for the FIB extraction process are found by particles slightly smaller than the average. All these effects can lead to a few percent reduced lattice constant for the in - as well as for the out-of-plane direction. The huge reduction in the out-of-plane direction is dominant and most likely attributed to the platinum cover layer, which leads to a compression of the c$_{MC}$-axis. On the other hand the mesocrystals are not destroyed by the extraction process and the structure is completely intact as can be seen in the scattering pattern.

---

129
Chapter 7  Diffraction from a single mesocrystal

Figure 7.8: Measurement of the (h0l) plane from $M'_{II}$ shows the presence of twin domains. Each color indicates peaks, which belong to one twin. A TEM picture on the left side visualizes the existence of such twins in a single mesocystal again colored in dependence of the orientation. This microscope picture was measured on a mesocrystal of the same sample. The zoom shows the splitting of one of the peaks suggesting several crystallites with slightly different lattice constants.

Looking at the lattice constant values extracted from the reflex position (see appendix table A.2), the values for the in-plane constants $a_{MC}$ from $M'_{C}$ of the (hhl) and (hhl) planes show that the difference of 0.04 nm is smaller than the error of 0.059 nm. The result of the same in-plane constant for 90° rotated planes proofs the tetragonal lattice. The difference in $c_{MC}$ between (002) and (004) reflexes is a systematic error that can occur through a shift of the peak fit position of (002) due to the influence of the FF slope on the Laue oscillations. For the mesocrystal $M'_{S}$ single peaks are visible, which are smearing out in one huge reflection. The lattice constant difference between the multiple peaks vary a few percent. The pictures of $M'_{S}$ (figure 7.7a, 7.7b) show a single crystal with a continuous distribution of lattice constants, while the pictures of $M''_{S}$ (see figure 7.8) shows additional peaks. The observation of both e.g. (101) and (01T) shows the presence of 180° twins, either resulting in peaks following $h+k+l=3n$ or $h-k+l=3n$. The colors red and cyan indicate peaks which belong to one twin with the corresponding parameters in table 7.2. This structure formation, which can be interpreted as stacking faults, is documented for these samples by TEM, made from a mesocrystal of the same sample (figure 7.8). The different colors inside the TEM picture mark twins with different orientations. The similar peak shapes of (0T1) and (01T), arising from the same twin, are consistent with this explanation. The peaks of one twin are split, suggesting that this twin is made up of three grains with different lattice constants, both out-of-plane and in-plane. These three peaks are separated from each other. The difference of the in-plane lattice constant is 5%, while the difference in c parameters is many times higher with 21%. This example shows
that there can be varying structural parameters within one single mesocrystal, not only in an ensemble as was expected from the GISAXS investigation.

The correlation length describes the average size of ordered domains. The peak width in $Q_z$- and $Q_y$-direction correspond to out-of-plane and in-plane correlations, respectively. In the case of the single mesocrystal, the measured correlation lengths are the value for one crystal and not an average over an ensemble. The crystal with cubic particles $M_{IC}$ shows a smaller in-plane correlation length $\langle \epsilon_{y\text{MC}} \rangle$ than the diameter measured with SEM (table 7.1), so the structure is not coherent through out the full diameter. A larger value for $\langle \epsilon_{z\text{MC}} \rangle$ than the height from the microscopy experiment indicates a correlation through the whole mesocrystal in the out-of-plane direction. The results of the single reflex rocking scan in appendix table A.2 show an influence of a lattice constant deviation and mosaic spread on the peak width. The increased $Q_y$-width of (00l) reflections with large $Q_z$-position can be explained by mosaicity around the beam axis ($\chi$) due to increased influences of the same tilting angle for a larger radius, while the broadening of the $Q_z$-width is influenced by the $c_{\text{MC}}$ lattice constant distribution. The comparison of the (101) and (301) reflexes of the (h0l) plane show only a small influence of a $a_{\text{MC}}$ lattice constant distribution. In contrast, the two single mesocrystals with spheres show broader peaks in comparison to the cubic one. A lesser degree of order is present, which is mainly manifested as a lattice constant distribution generating peaks which merge seamlessly indicating several grains. An influence from mosaic spread or a direction dependent lattice constant distribution is not clearly visible from the correlation length values. In contrast $M_{IS}$ shows distinct reflections which are more separated from each other indicating only a few grains with a large difference between their lattice constants.

### 7.3.1.3 Laue oscillation

The $M_{IC}$ crystal with cubic building blocks has sharp strong peaks (figure 7.9a) allowing a closer evaluation of the actual peak shape. The peak tails in $Q_z$ direction visible in logarithmic color scale, are Laue oscillations (see figure 7.9a inset), which indicate a high degree of order in the cubic sample, a flat surface and a relatively small and equal height. Oscillations in $Q_x$ and $Q_y$ direction are not visible due to the much larger size of the crystal in these directions and the limited correlation length discussed in the last subsection. The factor 20 between the diameter of 4.5 $\mu$m in comparison to 215 nm height would lead to 20 times smaller oscillations, which are not resolvable any more. Due to the cylindrical mesocrystal shape, the in-plane peak shape is a modified Bessel function (see equation 5.6 in section 5.1.1) instead of a Laue function. To proof that the shape actually resembles Laue oscillations and extract parameters like height and height distribution, a shifted Laue function in combination with a form factor, a particle size -, height - and lattice constant distribution and an incoherent background was used to fit the oscillations (see script in appendix section B.2). In the case of nanoparticles the form factor is important due to the relative size of the particles compared to the structure size and hence the influence of the oscillations on the scattering in comparison to atomic crystal. The atomic size distribution is not existing, while nanoparticles have typically a size distribution of a few percent. The used form factor with convoluted size distribution increases the Laue oscillations around $Q_z = 0$ in relation to the main peaks. The additional lattice constant distribution is required to describes the peak shape and oscillation amplitude. The result of the fit is shown in figure 7.10a. The model describe the scattering well and the present discrepancy is mainly introduced by the non-uniform background, which was described earlier and is not fit-able. The
Figure 7.9: Measurement of the (h0l) plane of a single mesocrystal with cubic particles. The zoom around the (002) reflection shows nice Laue oscillations, which could be reproduced with a simulation. The left inset shows a vertical line scan through the reflection.
7.3 Result and discussion

(a) Comparison of measurement and fit

(b) Influence of parameter variation on the fit function

Figure 7.10: Cross-section through the reflexes (101) and (101) in \(Q_z\) direction from figure 7.9a. The Laue oscillations are fitted with a Laue function in combination with a form factor, a particle size and lattice constant distribution and an incoherent background. The influence of a larger lattice constant distribution (\(\sigma_{c_{MC}}\)) and height distribution (\(\sigma_{N_L}\)) is shown in figure 7.10b.

asymmetry of the oscillation amplitude around the peaks can be induced by a distribution of lattices constants, which is observed in the reflectometry dataset from an ensemble of mesocrystals as well (see section 5.3.3). The derived lattice constant in out-of-plane direction of \(c_{MC} = 15.11\) matches the result from table 7.2 perfectly. The lattice constant distribution is with \(\sigma_{c_{MC}} = 0.85\%\) smaller than the in-situ GISAXS determined value from an ensemble of mesocrystals in an unfinished drying state of 1.5\%. For the in-situ GISAXS case it is assumed that the value will increase with longer drying time, so that the single mesocrystal lattice constant deviation found here is much smaller than for the ensemble average. This indicates a variation of lattice constants from mesocrystal to mesocrystal as has been proposed in earlier chapters. The influence of a higher distribution of \(\sigma_{c_{MC}} = 5.8\%\) (particle size distribution\(^1\)) is shown in figure 7.10b, where the peak shape gets broader and the oscillations smearing out to higher \(Q\). Such an asymmetrical broadening of the peak shape could be observed in reflectometry from an ensemble of mesocrystals where a lattice constant between different mesocrystals is expected (section 5.3.3). The number of repetitions of the unit cell is \(N_L = 13\), which result to a mesocrystal height of 196 nm. This value matches the result measured by the SEM (table 7.1) proving a fully coherent structure through out the whole mesocrystal. The distribution of the number of repetitions, which correspond to the height, is with \(\sigma_{N_L} = 0.3\) very small and confirms the observed flat mesocrystal from SEM (figure 7.2d). The influence of a higher height distribution is shown in figure 7.10b as red curve. A \(\sigma_{N_L} = 3\) suppresses nearly all oscillations, due to the different heights which are averaged. This is observed in an ensemble of mesocrystals, where the crystals have different heights and no oscillations between the GISAXS peaks are visible. The visible Laue oscillations makes this measurement unique, because normal crystals are too large to resolve such oscillations. In this experiment a perfect single crystal with a height in the 100 nm-range and 10 nm structure size is investigated, which allows the study of this peak shape. The results of the fit of the Laue oscillations are summarized in table 7.3.

\(^1\)The particle size distribution in the precursor solution is the order of magnitude for the lattice constant distribution expected when a mesocrystal would be formed by a random selection of particles.
sample ID | cMC [nm] | σcMC [%] | NL [cMC] | σNL [cMC]
--- | --- | --- | --- | ---
M_C: | 15.11 | 0.85 | 13 | 0.3

Table 7.3: Result of the Laue oscillation fit from the (101) reflection.

### 7.3.1.4 Simulation of the scattering pattern

The simulations in figure 7.9b for a perfectly ordered cubic system fit very well. A convolution of the cylinder form factor describing the mesocrystal shape with the reciprocal lattice including selection rules multiplied by the spherical form factor, the Lorentz factor and the Debye-Waller factor are considered. Additionally, an incoherent background is added. The resolution of $3.1 \times 10^{-4} \text{ Å}^{-1}$ determined earlier is used in this simulation. The shape and oscillations of the peaks introduced by the mesocrystal shape as a cylinder are in good agreement with the experiment using the height and radius from table 7.1. The mesocrystal shape influences mainly the simulated peak shape in Q_z direction, while Q_y is defined by the resolution function due to a µm sized crystal. A lattice constant distribution induced for example by a variation of the particle size, as well as existing mosaic spread are not considered, which explains the remaining difference to the shape, intensity and width of the measured peaks, especially for peaks at lower Q. The measurement method has no influence on the peak shape, only the intensity. A spherical form factor is used in this model due to the prohibitive computing time for the new rounded cubes FF model for $4 \cdot 10^5$ grid points. The problem arising from the FF imperfections is shown in the inset of figure 7.9b, where a too deep minimum in comparison to the measurement exists. On the other hand the used FF describes for example the absence of the structure factor allowed (103) reflex in the (h0l) plane. The Lorentz-factor (see section 2.2.4) used for the modeling tries to mimic the experimental conditions by assuming a constant scan rate in $\phi$ (normal Lorentz-factor, Q_y) and taking the maximum for the 5 measured positions in $\omega$ (Q_z direction). For example the (402) reflex which lies on a FF maximum with high intensity, is strongly suppressed by the scanning process. The effect is obvious when comparing a simulation with and without Lorentz correction (see appendix figure A.14). For the Debye-Waller factor an average displacement parameter $a_{DW} = 0.5 \text{ nm}$ is used. This simplified model describes the measured intensities quite well on the full Q-range. The simulation is described in section 5.3.1 in more detail and the python script and all simulations are attached in appendix section B.3 and section A.3.3.

### 7.3.2 Crystal structure analysis

#### 7.3.2.1 Rocking scans

To obtain integrated intensities of the reflections necessary for a quantitative structure analysis of a single mesocrystal, rocking scans of peaks of the cubic system for all accessed planes were performed. To achieve a well defined and optimized rocking scan of a reflection, the mesocrystal was aligned using the chi angle to bring the reflections in vertical direction. This way the omega angle could be used to scan the peaks perpendicular to their $\vec{Q}$ direction, thus the $\omega$-scan is equivalent to a scan in $\vec{Q}_x$ direction.
7.3 Result and discussion

Figure 7.12: Rocking scans for different peaks of the (h0l) plane of $M^l_C$. The grey line is the form factor of a perfect mesocrystal with defined sizes by SEM and shows the natural line shape. The filled curves shows a Lorentz function with HWHM determined at the $Q_y$-$Q_z$ plots, presenting the natural line shape of the present mesocrystal with limited correlation length. $F_{MC}(\theta)$ is the perfect mesocrystal form factor.

The integrated intensities are analyzed as follows: For each $\omega$ position two areas are chosen around one peak in the 2D-detector image (see figure 7.11). The smaller area defines the region, where a integration (sum) over the chosen area are taken and the large area excluding the integration region is used to extract the background by fitting a 2D parabola. The fitted background is then subtracted from the integration area prior to intensity extraction. With this method the integration works stable for all peaks, including those with low intensity. An example of the 2 dimensionally integrated intensity versus the incident angle $\omega$ for the (h0l) plane is shown in figure 7.12. These measurements are called rocking scans. The zero intensity far from the peak is an indication that the background subtraction works properly.

The peak shape and width of a rocking scans are defined by the energy and wavelength resolution of the experiment, the size and correlation length of the mesocrystal and the mosaicity. Mosaicity or mosaic spread is a property of macroscopic crystals which describes the average degree of tilting of lattice planes of structurally coherent regions against each other. Atomic crystals normally contain imperfections producing mosaic domains inside the structure which are misaligned against each other. To extract the mosaicity parameter from the measurement the half-width at half-maximum (HWHM) of the peaks have to be determined. Due to the asymmetric shape the HWHM can not be fitted and is calculated with the root mean square deviation.
Chapter 7 Diffraction from a single mesocrystal

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Table 7.4: Width of the rocking scan peaks measured on \( M_C^l \) determined by numeric calculation of the standard deviation.

(standard deviation SD). With this method the peak shape is not of importance. The results are shown in Table 7.4. The good energy resolution of \( \delta E/E = 0.5 \times 10^{-4} \) and the small divergence of the beam of 400 \( \mu \text{rad} \) in the present experiment is negligible.

At first we confine the analysis to the (00l) reflexes, which were measured in the (h0l) plane. For the same \( \chi \) and \( \varphi \) position for one plane, the width of the plotted (00l) reflections of one \( \omega \)-scans should be constant by pure mosaic spread. The discrepancy of the (002) and (004) parameters indicate an other influence on the peak width beside pure mosaic spread. The natural width given by the finite size of the mesocrystal can affect the rocking curve as it provides a finit peak width, which is constant in Q-space for all peaks. As has been described above, every \( \omega \)-scan is a transverse Q-scan perpendicular to the vertical and horizontal direction (for example for the (h0l) plane a scan in [0k0] direction). A finite broadening in [0k0] direction (e.g. Lorentz-function) yields a broadening of the \( \omega \)-scan. A \( Q_\parallel (\omega, Q_\parallel \rightarrow \omega, Q_\perp \rightarrow \omega) \) scan is different for reflexes at different \( \hat{Q} \) positions in the angle coordinate representation. In the case of small angles (\( \hat{Q} \) a flat Ewald-sphere), the contribution of the natural line shape to the width of the rocking curve is antiproportional to the value of \( Q_\perp \rightarrow \omega (\Delta \omega \propto \Delta Q_\perp) \). For the same step size in \( \omega \), the increments in \( Q \) are larger for peaks with higher \( Q \) value and consequently the width of the peaks in the \( \omega \) scan are smaller for higher \( Q \) values. Exactly this behavior is observed, the width of (002) is broader than for (004) reflexes (see Figure 7.12, Table 7.4). A transformation of the rocking scans from angle coordinates to Q space shows that the width of the peaks have the same order of magnitude for different reflexes (see Appendix Figure A.16), which is expected for the natural line shape contribution. Small differences show an influence of the mosaic spread and probably experimental imperfections not accounted for. An influence of the relatively large \( \omega \) step size has to be considered for reflexes with \( l > 3 \), for example (004) reflexes, and could explain the different peak shapes. It can be concluded that the shape and width of the rocking curves are mainly governed by the natural line shape of the mesocrystal. The influence of the mosaic spread is small. Additional structure next to the main peak suggests the presence of only a few big crystallites inside one mesocrystal. Plenty of small fragments would lead to a more Gaussian like peak shape and would have a smaller correlation length.

To indicate the influence of the natural line shape, the optimal mesocrystal form factor \( F_{MC}(\theta) \) (see 5.6) is plotted in Figure 7.12. The natural line shape is given by the perfect cylinder FF with size parameters extracted from SEM Table 7.1. It is obvious that the natural line shape of a perfect mesocrystal is much smaller than the measured curve. Plotting a Lorentz function with the HWHM determined for \( Q_\parallel \frac{\vec{a}^*}{2} \) at the \( Q_y-Q_z \) plots (see Table 7.2) shows that the determined
7.3 Result and discussion

Figure 7.13: Sketch of different mosaicity components. The rotation vector is in the viewing direction.

width from the other measurement geometry corresponds to the width of the rocking curve figure 7.12. This comparison confirms the statement that the natural line shape is the main determining factor. The deviation between theoretical line width of a perfect crystal and the measured curve of the present mesocrystal shows the existence of a limited in-plane correlation length, which is much smaller than the diameter of the mesocrystal. Discontinuities are present in the in-plane direction that limit the correlation of the mesocrystal structure.

The mosaic spread around the a-axis without the natural line shape can be calculated with the (00l) reflections for one crystal orientation. The influence of the natural width doubles from $|l|=2$ to $|l|=4$ reflexes and thus the difference between the mean square of (002) and (004) give the natural line shape part of $0.22^\circ$ for the (004) reflex in $\vec{b}$ direction. The difference between the (004) and the calculated line shape value yields a mosaic spread of $0.12^\circ$ in this direction, which rotates around the a-axis (horizontal axis) (see figure 7.13).

The c-axis mosaic spread can be estimated from the average value of the (101) and (011) reflexes. Using the above approach, the natural line shape of the (101) is $0.58^\circ$ calculated from the value of the (004) reflex. The mosaicity including an a- and c-axis component is $0.36^\circ$, which leads to an estimated c-axis mosaic spread of $0.52^\circ$. The other analyzed reflexes with an in-plane component (for example (112)) show higher values for the HWHM, which is an additional indication for a higher mosaic spread around the c-axis (see figure 7.13). That means that the average tilting of the crystallites around the vertical axis is higher than around the horizontal one. This result makes sense in consideration of the self-assembly process. The substrate provides a preferred direction for the ordering of the cubic particles, so it is more energetic favorable to order the planes parallel to the substrate. An a-axis mosaic spread of $0.1^\circ$ represents a tilting of crystallites to the substrate surface that corresponds to $1.7\text{ nm}$ distance to the substrate at one side of a $1 \mu\text{m}$ domain, which corresponds to the measured correlation length (see table 7.2). This distance matches the thickness of the organic shell (see section 4.1.2), which is reasonable, because the organic shell is soft and movable, while a higher tilting would not be energetically favorable due to the large gap.

In contrast, a higher mosaicity around the c-axis is not prohibited by the the self-assembly process. An in-plane tilting of crystallites against each other has no influence on the attachment to the substrate surface and needs less energy to be produced. Gaps, cracks and missing layers can produce such mosaics as shown in figure 7.14a obtained from an other mesocrystal. A shift
Chapter 7  Diffraction from a single mesocrystal

(a) Example for visible c-axis mosaicity
(b) Investigated sample M\textsubscript{C}

Figure 7.14: SEM pictures from top of mesocrystals of equivalent samples.

of 2 \degree between two crystallites is visible, probably produced by the drying process. Crystallites inside one crystal can result from discontinuities like in an atomic crystal. In the case of a self-assembled nanoparticle superstructure the drying process as an additional factor is relevant for the formation of bent lattice planes and cracks leading to crystallites separation, which both produce mosaicity. In contrast to the tilting due to cracks as seen in figure 7.14a the weaker bending effects of nanoparticle rows inside one crystallite without a crack are not visible on this small length scale. The higher flexibility in the mesocrystal structure differs strongly from atomic crystals, where every crystallite has a rigid lattice. Due to soft bondings between the nanoparticles, lattice planes can be sheared or bent against each other caused by the stress during the drying process or other pressure effects. For a crystals composed of nanoparticles it is energetic favorable to build the special superstructure, but the energy cost for deformation is relatively low.

A comparison with a SEM picture taken before extraction from the top of the investigated single mesocrystal showed no measurable shears or crystallites inside the mapped area. Figure 7.14b illustrates this with the aid of red lines. The determined mosaic spread around the c-axis of 0.52 \degree should be hardly measurable with SEM as it would be in the order of a pixel over the full length of the red lines. A shearing effect over a long range or a few crystallites with very low tilting against each other can lead to the measured c-axis mosaic spread. The quantitative results of the rocking scan analysis are summarized in table 7.5 and overall the investigated mesocrystal shows an excellent structural coherence considering all possible influences described above. The existence of mosaicity cannot be established by GISAXS because an average over an ensemble of mesocrystals, rotated against each other, is present.

<table>
<thead>
<tr>
<th>sample ID</th>
<th>a-axis mosaicity [\degree]</th>
<th>c-axis mosaicity [\degree]</th>
<th>natural line shape of (004) [\degree]</th>
<th>natural line shape of (10\text{T}) [\degree]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M\textsubscript{C} :</td>
<td>0.12</td>
<td>0.52</td>
<td>0.22</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 7.5: Result of the rocking scan analysis for mosaicity. The a-axis component is determined from the (00l) reflexes and the c-axis component from the (10\text{T}) reflexes, both from the (h0l) plane.
7.3 Result and discussion

(a) Integrated intensities for different points in reciprocal space to show the high scattering of the intensities. The grey line is a spherical form factor with the values determined by SAXS.

(b) Comparison of different FF models (solid lines) with the averaged integrated intensities (data points).

Figure 7.15: Integrated intensities of $M_C^I$.

### 7.3.2.2 Integrated intensities

For the previous analysis of the rocking scans (2 dimensionally integrated intensities) only vertical reflections were considered\(^2\). Due to the low statistics, other peaks from the same measurement are used for the integrated intensity analysis in addition. In this case $2\theta_h$ is not equal to zero ( $2\theta_h$ is the scattering angle component perpendicular to $\vec{\omega}$). As an example, for $\chi = 0$ $2\theta_v$ corresponds to the $Q_z$ direction and $2\theta_h$ to the $Q_y$ direction. For the integration of the rocking curves the trapezoidal rule is applied. Simple summation as well as Simpson’s rule integration have been tried as well, but did not yield much different results. A Lorentz factor (see section 2.2.4) correction is made in dependence on $2\theta_v$. Through this approach several redundant intensity values are collected for the same reflection. The integrated intensities versus $|\vec{Q}|$ for different reciprocal lattice planes are shown in figure 7.15a and in table A.3-table A.11, where a large variation of intensities is observed for every equivalent peak. This points out the challenge of measuring a µm-size crystal with a µ-focus beam. Due to the limited positional accuracy the translation motors needed to be realigned for each $\chi$ orientation\(^3\). This alignment, however, will never result in exactly the same photon density because of beam inhomogeneities in horizontal direction, which were measured in a translation scan (appendix figure A.17). To make a comparison with a possible model the average of the intensities of all equivalent peaks is used. For each set of symmetry equivalent reflections, the error is calculated as the standard deviation of all measured points.

The extracted structure factors allow a direct comparison with a model based on the I4/mmm structure discussed in section 7.3.1. The body centered tetragonal (bct) structure with only one particle in its basis (2 per unit cell at (0,0,0) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$) leads to no intensity variation (except for the selection rules) from the unit cell part of the structure factor, thus the peak

\(^2\)Vertical means that the scattering plane normal is parallel to $\vec{\omega}$ and therefore the scattering angle $2\theta$ has only a vertical component (called $2\theta_v$).

\(^3\)The changes in $\chi$ can be as big as 180°.
Chapter 7 Diffraction from a single mesocrystal

### Table 7.6

<table>
<thead>
<tr>
<th>Model</th>
<th>$I_0$</th>
<th>$a_{NP}/2r$ [nm]</th>
<th>$\sigma_{a_{NP}}/a_{NP}$ [%]</th>
<th>$\tau$</th>
<th>$a_{DW_{MC}}$ [Å]</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rounded cubes:</td>
<td>$(13 \pm 2.3) \cdot 10^{-9}$</td>
<td>10.8 $\pm$ 1.4</td>
<td>0.45 $\pm$ 5</td>
<td>0.85</td>
<td>$0.001 \pm NaN$</td>
<td>24.43</td>
</tr>
<tr>
<td>Truncated cubes:</td>
<td>$(9.3 \pm 1.6) \cdot 10^{-10}$</td>
<td>8.6 $\pm$ 0.4</td>
<td>0.65 $\pm$ 52</td>
<td>0.6</td>
<td>$7.44 \pm 4.12$</td>
<td>44.62</td>
</tr>
<tr>
<td>Spheres:</td>
<td>$(28 \pm 3.9) \cdot 10^{-9}$</td>
<td>12.0 $\pm$ 0.1</td>
<td>0.2 $\pm$ 1</td>
<td>1</td>
<td>$0 \pm NaN$</td>
<td>16.63</td>
</tr>
<tr>
<td>SAXS (rounded cubes):</td>
<td>$(430 \pm 2.8) \cdot 10^{-11}$</td>
<td>10.8 $\pm$ 0.02</td>
<td>5.9 $\pm$ 0.5</td>
<td>0.775</td>
<td>/</td>
<td>138.4</td>
</tr>
<tr>
<td>SAXS (spheres):</td>
<td>$(920 \pm 5) \cdot 10^{-11}$</td>
<td>12.22 $\pm$ 0.02</td>
<td>7.4 $\pm$ 0.3</td>
<td>1</td>
<td>/</td>
<td>299</td>
</tr>
</tbody>
</table>

Table 7.6: Fit parameters of the models shown in figure 7.15b. The parameters without error have not been fitted, errors with NaN denote numerical problems in the error calculation.

Intensity must be described by the directional dependent form factor and possibly a Debye-Waller contribution.

Consequently the discussion in section 4.1.2 needs to be resumed as the rounded cubes and the spherical form factor, indistinguishable in the directionally averaged SAXS measurements, lead to notably different structure factors in the ordered case. It is expected that the particles are aligned with respect to the mesocrystal lattice so the directional average is not the correct description any more. Therefore a spherical form factor (equation 5.3) is compared to the analytical directional truncated cubes form factor (equation 5.4) and the numerical directional rounded cubes form factor (equation 5.5). The truncated cubes FF with edge length $a_{NP}$ and degree of truncation $\tau_{Trunc}$ describes a flat truncation and makes a cubeoctahedron for the highest degree of truncation. The rounded cubes FF on the other hand with edge length $a_{NP}$ and degree of truncation $\tau_{Round}$ describes a spherical truncation and produces a perfect sphere for the highest degree of truncation. The real space representation of the two kinds of cubic form factors in real space and different degree of truncation are shown in figure 5.1. A distribution of the particle size and an isotropic Debye-Waller factor term which involves the information about the average displacement of the lattice position is included in all fit models. The python script is attached in section B.1.

The best fit result of all form factor fit functions including size distribution and Debye-Waller factor are shown in figure 7.15b, table 7.6 and table A.12. Fitting parameters have been the edge length $a_{NP_{MC}}$, the Debye-Waller factor average displacement $a_{DW_{MC}}$ and the particle size distribution $\sigma_{a_{NP_{MC}}}$ (log normal - integral over different FF of different sizes). $\tau_{Trunc_{MC}}$ or $\tau_{Round_{MC}}$ were fixed for one fit but have been varied manually. For a better comparison, the intensity scale is plotted in $I \cdot Q^4$. The rounded cube model describes nearly every measured point well for every direction within the error bars, while the truncated cube model shows strong discrepancies for some points. The spherical form factor describe the data well at low Q, but shows expected discrepancies at higher Q, as small changes in the shape mostly manifest themselves at higher Q values. Within the limit of the error bars, the rounded cube model describes the data best. Although the $\chi^2/R_1$ value for the spherical form factor is slightly lower than for the rounded cubes case, the latter can still be considered the best suited FF as it better describes the SAXS data (figure 4.2) and still incorporates the cubic facets visible in e.g. TEM images. The flat truncated model does neither fit the single MC diffraction, nor the SAXS data very well.

To clarify the difference between these models and the point where the model does not fit well, complete FF’s in different crystallographic directions were calculated using the resulting fit parameters. This is done for the spherical, truncated and rounded cubes model. A selection of the results can be seen at figure 7.16, all pictures for different $\tau$ can be found in appendix.
7.3 Result and discussion

(a) Truncated cubes model with $\tau_{\text{Trunc}} = 0$
\[ a_{NP_{MC}} = 8.27 \pm 0.0\%, \quad a_{DW_{MC}} = 0.50 \text{ nm} \]

(b) Rounded cubes model with $\tau_{\text{Round}} = 0$
\[ a_{NP_{MC}} = 8.20 \pm 0.0\%, \quad a_{DW_{MC}} = 0.007 \text{ nm} \]

(c) Truncated cubes model with $\tau_{\text{Trunc}} = 0.8$
\[ a_{NP_{MC}} = 8.69 \pm 3.8\%, \quad a_{DW_{MC}} = 0.00 \text{ nm} \]

(d) Rounded cubes model with $\tau_{\text{Round}} = 0.85$
\[ a_{NP_{MC}} = 10.78 \pm 0.4\%, \quad a_{DW_{MC}} = 0.00 \text{ nm} \]

(e) Analytical spherical FF

(f) Rounded cubes model with $\tau_{\text{Round}} = 1$
\[ a_{NP_{MC}} = 12.01 \pm 0.0\%, \quad a_{DW_{MC}} = 0.00 \text{ nm} \]

Figure 7.16: Results of fits from the truncated cube and the rounded cube model. Figure 7.16a and 7.16b fitted for a perfect cube and figure 7.16e and 7.16f for a perfect spherical particle shows the correctness of the new rounded cube model. The best parameters for the respective models are shown in figure 7.16c and 7.16d.
A.18 and A.19. For a better comparison the intensity scale is plotted in $I \cdot \vec{Q}^4$. The scale of the Debye-Waller factor term, which is included in the fit, is plotted linearly on the right y-axis. Different colors present various Q-directions.

**Figure 7.16c and 7.16d** show the results for different $\tau$’s for both direction-dependent FF’s. It is obvious that the model with the rounded cubes describes the data well for every direction within the error bars, while the truncated cubes model could not describe the scattering in the direction of the edges. The results from figure **figure 7.16** make it obvious, that it is important to use a direction dependent form factor to correctly describe the peak intensities for the 3D nanoparticle assemblies. In contrast to the perfectly isotropic scattering potential of spheric particles the cubes have a directional dependence in the form factor, which needs to be considered when the particles have a defined orientation in the mesocrystal unit cell. A GISAXS pattern of an ensemble of mesocrystals contains the information about the direction dependent form factor as well, but the modeling of the intensities needs to be performed using DWBA which is far more complicated and requires additional information (see section 5.3.4).

The shape differences between the truncated and rounded cubes in the direction of the edges leads to sizable changes in the scattering for example for the \{hh0\} and \{2hhh\} directions. In the rounded case not only the corners get truncated, but the edges as well, creating an additional facet responsible for additional intensity in the diagonal \{hh0\} directions. The shape of the rounded cube model reproduces the HRTEM pictures well (see **figure 4.3** in section 4.1.2). The new fits confirm the results of the SAXS measurement, where the truncated cubes FF does not match the data and shows that the flat facets do not describe the present particles. The SAXS experiment cannot distinguish between shapes with small differences due to the integration over all directions. It is dominated by the most intense scattering of the \{h00\} direction, which has the smallest difference between all models.

The comparison between the analytical and the numerical form factor model with FFT shows no difference between the fits for a perfect cube ($\tau_{\text{RoundMC}} = \tau_{\text{TruncMC}} = 0$) (**figure 7.16a, 7.16b**). The other extreme case of the rounded cube model is shown in **figure 7.16f**, where a perfect spherical particle is simulated. All directions are similar and follow the analytic sphere (**figure 7.16e**). The new model can reproduce a perfect spherical and cubic system equivalent to the analytic models showing the applicability of the numeric approximation. The snaphy shape of the model is a result of the interpolation used to extract the intensity from the regular grid of the calculation.

The result of the fit with the rounded cube model has an edge length of the cubes $a_{\text{NP},MC}$ of 10.78 nm, a size distribution of 0.4%, a truncation $\tau_{\text{RoundMC}}$ of 0.85 and no notable Debye-Waller factor (isotropic, $a_{\text{DW}} = 0$ nm). The value of $\tau_{\text{RoundMC}}$ confirms the results of the SAXS fit (see chapter 4 in table 4.2). The used nanoparticles are not perfectly cubic but have strongly rounded edges and small flat facets in [100] directions (see **figure 7.17a**). With this experiment we could show that highly truncated nanocubes self-assembled in a body-centered tetragonal (bct) arrangement inside one mesocrystal.

The absence of a Debye-Waller term shows that the changes from the perfect lattice position are immeasurable small, although small differences in the form factor can lead to a similar influence

\[\text{Which we can assert with large confidence as it is present at the surface measured by SEM and is a prerequisite for self organization in non closed packed structures.}\]
7.4 Conclusions

This challenging experiment proved the feasibility of the investigation on single, small mesocrystals of nanoparticles to open a new field for further investigations of the mesocrystal properties. With the outstanding intensity and precision of state of the art synchrotron beamlines it is possible to push the already established limits in diffraction from Å-size \([39, 57, 78, 79]\) and nm-size unit cells \([62, 97]\) further to 10 nm large building blocks with samples of only 2.5 \(\mu m^3\) scattering volume. So far the smallest crystals investigated for the atomic structure are reported with volume in the \(10^3 \mu m^3\) range \([16, 17, 48]\). The achievable data quality is, as expected, not yet comparable to conventional single crystal XRD, as is obvious for the integrated intensities. Nevertheless a lot of new information could be gained complementary to GISAXS on a 2D powder sample.

The space group analysis is consistent with the structure deduced from the ensemble of mesocrystals, \(R\bar{3}m\) for spheres and \(I\bar{4}/m\bar{m}\) space group for crystals build from cubic nanoparticles. A
quantitative structure analysis of a single mesocrystal with GISAXS was not possible before as the Born approximation does not apply. Furthermore it was not clear if the GISAXS measurement from an ensemble of mesocrystals masks the real structure of a single one as the single crystals are rotated against each other (2D powder). A measurement of the related reciprocal lattice planes is only possible in this experimental configuration without averaging intensities from hundred thousand of probably different mesocrystals and without the need to apply the DWBA to the modeling.

The images from different planes show the high degree of order in these mesocrystals and that 2 out of 3 investigated samples are actually single crystals. The other closed packed mesocrystal shows a twin with reversed structure, as results of stacking faults in the nearly closed packed structure. The correlation length measured at one mesocrystal for the out-of-plane direction is the height of the crystal, while the in-plane value is smaller. This knowledge about the structural correlations of one crystal is not measurable in the 2D powder. Additionally it is shown that these crystals differ in the lattice constants from the ensemble average, which is attributed to a tendency of similar particles to assemble in one mesocrystal.

All findings about the reflex shape can be fully explained with a Born approximation model of a single crystal with little in-plane mosaic of around 1 µm size. A micro-strain effect (variation of lattice parameters) as well as a small mosaicity can be observed. The presence of different lattice constant in different grains of one mesocrystal can be seen nicely in the spherical mesocrystal, where a few distinct peaks are visible. A small lattice constant distribution in out-of-plane direction could be observed in the cubic crystal as a broadening effect and as influence on the Laue oscillations, as well. The rocking curve analysis shows the existence of a few big mosaics inside the mesocrystal and a different mosaicity for different directions. The a-axis mosaic spread of 0.1° and the c-axis mosaic spread of 0.5° are quite small for this new crystal system and have a comparable quality to atomic crystals. According to P. Jeffrey [109] crystals are considered good with a mosaicity of 0.2° or less and bad with a mosaic spread with 1.0° or more. The comparison to small crystals, which have been reported to have large mosaic spread of 0.5-1° or more [16], shows that the new crystal system has very good mosaicity values especially when one considers the soft bonding between the nanoparticles and the nanoparticle size distribution. The higher average tilting of the crystallites around the vertical compared to the horizontal axis makes sense in consideration of the gravity and van-der-Waals attraction to the silicon pulling towards the substrate during self-assembly. Tilting in the plane does not produce such a problem.

Crystals with nanoparticle building blocks have special properties, which influence the formation of crystallites and their nature. On the one hand crystallites can develop with stacking faults (closed packed structure), cracks or other defects like in atomic crystals, but the weak bond between the particles and the flexible distance due to the organic shell of the nanoparticles can lead to shearing and bending of lattice planes within one crystallite. The crack and stacking fault formation during the growth process could be observed in SEM, as well. The size distributed nanoparticles in contrast to perfectly equal atoms, can order together by size and lead to grains inside one mesocrystal with different lattice constants. A continuous lattice constant distribution in the c-direction can be produced by e.g. curved planes caused by the stress from the cutting process at the edges of the crystal.

The existence of Laue oscillations is another unique observation in this measurement, because normal crystals are too large to resolve oscillations and typically non uniformly shaped. In this
experiment a perfect single crystal with a height of 215 nm is investigated which makes this phenomenon observable. Averaging over a lot of heights from different mesocrystals in the GISAXS experiment destroys these oscillations. The complexity of a system of nanoparticles can be seen in the fit of the Laue oscillations, where the Laue function, a form factor, size-, height - and lattice constant distribution needs to be considered to fully describe the system. In contrast to the GISAXS case where only correlation lengths could be extracted, this fit allows us to deduce the real height of the mesocrystal which perfectly matches the SEM observation. In addition, this allowed us to fit a height and lattice constant distribution, which both are found to be small.

The results of the 2D simulations of the single crystal pattern confirms the developed model (section 5.1.1) and the understanding of the described features of the scattering pattern. The cylindrical form factor for the mesocrystal describes the observed Laue oscillations and shape of the peak and the used nanoparticle form factor together with a Lorentz factor explains the pattern well.

The new model of the direction dependent rounded cubes form factor describes the integrated intensity well. From the comparison of the observed intensities with radial symmetric and directional form factors it is clear that the structure factor can only be described with a directional dependence in the cubic case. This implies that the orientation of the nanocubes within the mesocrystal unit cell is aligned to the unit cell axes as excepted from the unit cell symmetry. This is supported by the TEM images in chapter 4, too. An analytical spheres FF, as well as the truncated cubes form factor do not describe the structure factor as good. The directional dependence of the FF non parallel to the [H00] directions is strongly dominated by the fine shape differences at the edges, which yields a strong difference between the truncated and rounded model. This sensitivity is lost in the orientational average of a SAXS experiment.

The good agreement of the form factor fit with a size distribution of 0.4% and the fact that the cube edge length $a_{NP}$ is lower than the average value derived from SAXS shows quantitatively that particles with very similar shape and size tend to form one mesocrystal. A shape-selective self-separation process during the self-assembly of the superstructures was already indicated with microscopy analysis by Song et al. [86], but in this work additionally to the relatively coarse SEM analysis we have analyzed this effect more quantitatively and with full bulk sensitivity using scattering. During the crystal growth it is energetically favorable to grow crystal with the same size and shape to reduce defects like dislocations or stacking faults. This new information has not been obtained by GISAXS on an ensemble of mesocrystals, because every mesocrystal has its own small size distribution but the experiment yields an average over a lot of different average sizes from different mesocrystals, which mask the quality of a single one.

All together the single mesocrystal is an almost perfect crystal system with typical crystalline defects. The extraction of a single mesocrystal using focused ion beam techniques and the investigation with a microfocus x-ray beam shows the high stability of these mesocrystals. The investigation of a separated crystal gave a new quantitative insight into some structural parameters not accessible in a sample containing a mesocrystal ensemble.

A first attempt of wide angle-diffraction on a single mesocrystal was tried to search for preferred crystal orientations of the nanoparticles inside one mesocrystal. A subsequent estimation of the expected intensity shows that only $1 \times 10^{-3}$ c/s can be expected, which is not feasible. A reduction of the background with for example a completely evacuated fly path could probably enable this type of experiment.
Chapter 8

Conclusion and outlook

In this PhD thesis, a very detailed and profound structural characterization of the 3D assemblies of magnetic nanoparticles is presented. The process of self-assembly and its properties have been analyzed with in-situ and post-deposition characterization. The combined results of these experiments have led to a possible explanation of the self-assembly process; a detailed model is also included.

Well-characterized $\gamma$-Fe$_2$O$_3$ nanoparticles were used as basic materials [14, 34, 52, 103], which self-assembled on silicon substrates under well-controlled preparation conditions resulting in an ensemble of mesocrystals distributed over the surface. Each mesocrystal is a three-dimensional, highly-ordered periodic arrangement of nanoparticles. It was possible with the combined effort of local microscopy and global diffraction experiments to find the optimal deposition conditions to produce high-quality nanoparticle superstructures. In this thesis, particular attention was given to the characteristics of the ensemble of mesocrystals and their self-assembly as well as of a single mesocrystal, which was investigated by a challenging diffraction experiment.

The microscopy methods applied yield important information, such as the height, shape and surface coverage of the mesocrystals (AFM). They visualize the nanoparticle superstructure, the existing material and larger structures in $\mu$m size on the surface (SEM) and inside the crystals (TEM). Additionally, selected area electron diffraction was performed to determine the atomic structure and the preferred crystalline orientation inside a small area of the assembly. For a depth-resolved structural characterization over a large sample area, scattering experiments were carried out. Basic information, such as the knowledge of the morphology of individual nanoparticles was obtained by SAXS and a new form factor model for the cubic particles was applied successfully. The nanoparticle superstructure in the ensemble was primarily investigated by GISAXS in-situ time-dependent or after deposition. These experiments shed light on the averaged structure of the ensemble of mesocrystals in terms of space group, lattice constant distribution, correlation length or crystal tiltings. Complementary to the SEAD experiments, the crystalline orientations in the assemblies averaged over the ensemble were analyzed by diffraction measurements at the x-ray reflectometer and the four circle diffractometer. To get an insight into parameters otherwise masked by the ensemble average, a diffraction experiment was performed on a single separated mesocrystal. In this configuration, a quantitative structure analysis could be made. Although this experiment alone yields interesting results concerning the structural quality and coherence of a single mesocrystal, it was found once again that the combination of different methods allows the development of a detailed structural and growth model.
Chapter 8 Conclusion and outlook

The structure model describing all results coherently is an ensemble of mesocrystals with an arbitrary in-plane rotation and a preferred c-axis orientation parallel to the substrate’s normal (2D powder). A single mesocrystal itself is an approximately cylindrically shaped crystal consisting of particles with extremely narrow size distribution. It is only possible for the particles to make small, local deviations from the perfect lattice position. The coherence of the structure in the best samples is limited only by the mesocrystal boundaries; stacking faults were found in the case of spheric particles. Crystals with nanoparticle building blocks have special properties which influence the formation of crystallites and their nature. On the one hand crystallites can develop with stacking faults (closed packed structure), cracks or other defects as in atomic crystals, but the weak bond between the particles and the flexible distances involved, due to the organic shell of the nanoparticles, can lead to the shearing and bending of lattice planes within one crystallite. A continuous lattice constant distribution in the c-direction can be produced e.g. by stress on the edges of the crystal or gravity pulling towards the substrate.

If we consider the complete ensemble of mesocrystals growing independently, a lot of inhomogeneity of the mesocrystal 2D powder has to be taken into account, which introduces additional complexity to the model and leads to peak broadening, for example, which masks the “true” physical characteristics of the structural order. One of the properties of the ensemble statistic is the out-of-plane rotation (c-axis tilted with respect to the substrate surface normal) of the individual mesocrystal, which could be observed in microscopy images and is connected to the radial smearing of the peaks in the GISAXS patterns. This phenomenon was often found in samples produced with a shorter solvent evaporation time. The quantitative space group analysis, which is only possible in the single mesocrystal configuration, is consistent with the analysis from the GISAXS pattern measured on the ensemble. The space groups determined are R̅3m for spheres and I4/mmm for crystals consisting of cubes. In samples with very good mesocrystal structures, it is even observed that the mesocrystals have facets defined by the unit cell geometry (30/60° angles for the closed packed spheres and 45/90° for the cubic system). Diffraction measurements show that the anisotropic cubic shape aligns the individual particles to the mesocrystal lattice so that a preferred crystal orientation was found, which was absent in the case of spheres. The observed size distribution of the mesocrystals inside the ensemble has an obvious effect on the measured scattering pattern in comparison to the single mesocrystal diffraction patterns. The incoherent average of an ensemble of Gaussian-size distributed mesocrystals in a GISAXS pattern shows distorted peak shapes and blurred peak tails, while for the single mesocrystal, Laue oscillations are clearly visible.

The observations used to develop this structural model indicate a property of the mesocrystal ensemble which helps to understand the self-organization process itself. As single mesocrystals have been found to have a smaller particle size and lattice parameter distribution than free particles in solution and in 2D mesocrystal powder samples, the particles must form mesocrystals in a shape-selective process. This is visible in the GISAXS patterns as the lattice constant distribution between the individual mesocrystals broadens the peaks with respect to a single mesocrystal as they are the sum of several peaks with different positions. Also in the in-situ experiment at the beginning of the nucleation, it is clear that the peaks which grow broader over time are made up of narrow peaks. The size and shape-selective self-separation process during the self-assembly of the superstructures was already indicated in the microscopy analysis by Song et al. [86], but in this current work additional to the relatively coarse SEM analysis, we have analyzed this effect more quantitatively and with full depth resolution using scattering methods. Combining the results from our attempts at structure determination and in-situ obser-
vations during the growth phase, the model of the self-organization process was developed.

In general, evaporation-induced mesocrystal growth can be divided into four stages: vertical droplet reduction, the highly concentrated film, the nucleation and the drying stage, whereby only the third stage was found to be important for the structure formation and is described in the model. Whether the first two stages are relevant for good order, or whether only the nucleation stage itself was of importance, could not be revealed with the experiments performed. Mesocrystal growth occurs in the dense solution when a critical concentration is reached at the substrate-liquid-air interface, verified by the in-situ GISAXS measurement. SAXS measurements at different heights of the droplet during evaporation show neither cluster formation at the droplet surface, nor nucleation in the droplet volume. This result supports a process as described by Siffalovic et.al. [83] for nanoparticle ordering at the three-phase contact line (TPCL). When a critical concentration is reached at the drying front where separated particles, movable via Brownian motion, accumulate on the substrate and reach a sufficiently low distance to get attracted by the van der Walls force between substrate and particles, then cluster formation can occur. The particles assemble size- and shape-selective, as the growth of similar particles minimizes the surface energy. Nucleation areas develop as highly-ordered 2D nanoparticle assemblies on the substrate, which are connected by less ordered particles of different shapes. Three-dimensional mesocrystal growth takes place in these highly ordered regions with matching nanoparticles. The particles start to order in the confined 3D arrangement, due to the finite area of nucleation and a finite diffusion length. This selective growth pattern is the reason for the formation of separate mesocrystals. Nanocrystals which do not find a match continue to move around to find a vacancy in a mesocrystal or sediment on the ground as residual particles. When compared to the atomic thin film growth, a similarity to the Volmer-Weber growth is observable [19], but some new aspects, such as the distribution of the size and shape of nanoparticles must also be considered. For the areas with extremely different particles and hence more disorder, a good template to provide a crystalline growth is missing. At the end of the self-assembly process, an ensemble of separated mesocrystals is generated, covering all the nucleation areas.

In addition, the influence of different deposition parameters on this process has been investigated. As can be expected from the diffusion-dependent size separation, evaporation time was found to be very important for a good structural quality, as the particles need to be able to find suitable vacancies. Although the time particles spend in the free solution seems to have no influence in terms of self-organization, slower evaporation leads to decreased movement of the TPCL, where the ordering is supposed to take place. In addition, the reduced drying rate can lead to a reduction of crack formation and similar effects that reduce the structural quality of mesocrystals after growth has finished. Different magnetic field arrangements can either support or hinder this process depending on the field strength and direction as well as gradient. The best nanoparticle superstructure is obtained for an upwardly-pointing magnetic gradient configuration. No sizable effect of the dipole-dipole interaction between the particles on the formed mesocrystal structure was found unless very extreme conditions were applied (e.g. a field gradient of 70 mT/cm). In a very strong gradient field a macroscopic polycrystalline particle assembly in the mm-range was formed, following the field lines. Similarly, a strong in-plane field leads to elongated mesocrystals (≈ hundred µm in length) along the field lines. The systematic parameter variation allowed the selection of the best deposition conditions for the given system, which will be of great importance for future experiments.

Although many qualitative statements about structure and self-organization models can be made directly from experimental observations, many differences could only be quantified from the

149
modeling of scattering intensities. Different approaches to the intensity simulation from the structure model described here have been derived and optimized for the given application. The good agreement between measured and simulated peak shapes supports the confidence in the structure model.

In Summary, many new scientific findings have been gathered from observing the process of self-assembly and the structural properties of the ensemble of mesocrystals and of a separated single mesocrystal consisting of magnetic nanoparticles. New and challenging experiments were performed, allowing novel insights only possible using modern scattering techniques. A first model for the complex structure of the ensemble of the mesocrystal, as well as a model for the self-organization process has been developed.

This knowledge provides several basic requirements for the construction of new and almost perfect model systems for the subsequent investigation of the magnetic correlations inside a nanoparticle superstructure. The new magnetism reflectometer MARIA at MLZ in Garching, capable of measuring GISANS with polarized neutrons, as well as the new small-angle diffractometer D33 at ILL in Grenoble, will lead to new possibilities for the analysis of information on magnetic moments averaged over the entire nanoparticle arrangement and the correlations between adjacent particles, respectively. The first experiments studying the magnetic properties have been performed with scattering methods and will be published separately.
Appendix A

Additional Figures and Tables

In this chapter additional figures and tables are given. The context and descriptions can be found in the corresponding chapters.

A.1 Appendix for chapter 4

![Image](image1.png)

(a) The residual particles on the ground layer

**Figure A.1:** Illustration of characteristics of the mesocrystal self-assembling.
Figure A.2: Illustration of characteristics of the mesocrystal self-assembling.

(a) Perpendicular edges of mesocrystals.

Figure A.3: SEM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up ($D_{5.01}^{1.68, 80}$).

(a) Small mesocrystals and ground layer
Figure A.4: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up ($D_{S,5.01}^{1.68,1.80}$).
Figure A.5: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up ($D_{8.5,0.01}$).
Figure A.6: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient down (D_{LS, 5.01}^{Lg1. 68y > 80}).
Figure A.7: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient down (D_{Lg,68\%80,S,5.01}).
Figure A.8: SEM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under different field conditions.
Appendix A: Additional Figures and Tables

Figure A.9: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient in-plane configuration \((D_{S,5.01}^{-1})\).
Figure A.10: AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient in-plane configuration (D_{S,5.01}^{-1}).
**Figure A.11:** Ensemble of mesocrystals formed from spherical building blocks self-assembled with different evaporation times for a gradient in-plane configuration.
A.2 Appendix of chapter 6: Time evolution of mesocrystal growth
### Table A.1: Example fit parameters of the time-resolved in-situ GISAXS study. The errors are small as they are only numerical results from the fitting algorithm.
A.3 Appendix of chapter 7:  
Diffraction from a single mesocrystal

A.3.1 Scattering patterns

The scattering patterns on the following pages show additional measurements from different reciprocal lattice planes of the samples investigated.
Figure A.12: Diffraction pattern from single mesocrystals with cubic or spherical building blocks for different crystalline planes.
A.3 Appendix of chapter 7: Diffraction from a single mesocystal

Figure A.13: Diffraction pattern from single mesocrystals with cubic building blocks for different crystalline planes.
A.3.2 Lattice constant and correlation lengths

In the following table the individual values of lattice constants and correlation lengths from different reciprocal lattice planes are listed.
A.3 Appendix of chapter 7: Diffraction from a single mesocrystal

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<th>$c_{MC}$ [nm]</th>
<th>$\varepsilon_{2MC}$ [nm]</th>
<th>$\varepsilon_{zMC}$ [nm]</th>
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Table A.2: Lattice constants and correlation lengths taken from reflexes of different reciprocal lattice planes of the single mesocrystal measurements. The values are averages of two individual peaks at positions mirrored at the origin to remove any effect from an imperfect determined zero position. Reflexes with two well separated peaks have two values, one for each individual peak.

A.3.3 Simulations

The scattering patterns on the following pages show simulations of the single mesocrystal diffraction.
Figure A.14: Calculated diffraction pattern from single mesocrystals with cubic building blocks for the (h0l) plane. The influence of the Lorentz factor is shown by comparison of simulations with and without consideration.
Figure A.15: Calculated diffraction pattern from single mesocrystals with cubic building blocks for the (hhl) plane. The influence of the Lorentz factor is shown by comparison of simulations with and without consideration.
A.3.4 Rocking scans and integrated intensities

The plots on the following pages show rocking scans in Q space, additional fits of the integrated intensities with different parameters and tables with integrated intensities.

Figure A.16: Rocking scans for different peaks of the (HOL) plane of $M_i^c$ in Q space. The peak width are obviously very similar, showing a small influence of the mosaicty on the measured shape.

Figure A.17: Translation scans of the (100) and (001) reflections to measure the homogeneity/inhomogeneity of the beam. The curves with dark color are scans over the beam height and show sharp peaks which indicate a small beam. The lighter color plots are scans over the beam width, which show a large and inhomogeneous beam in this direction.
### Table A.3: Integrated intensities of symmetry equivalent reflexes of (002) at a Q position of 0.083 from $M_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

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### Table A.4: Integrated intensities of symmetry equivalent reflexes of (004) at a Q position of 0.165 from $M_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

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### Table A.5: Integrated intensities of symmetry equivalent reflexes of (101) at a Q position of 0.062 from $M_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

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### Appendix A Additional Figures and Tables

#### Table A.6: Integrated intensities of symmetry equivalent reflexes of (110) at a Q position of 0.066 from $M_{IC}$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

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</tbody>
</table>

#### Table A.7: Integrated intensities of symmetry equivalent reflexes of (112) at a Q position of 0.106 from $M_{IC}$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>plain</th>
<th>$\chi$ [°]</th>
<th>$I$ [a.u.]</th>
<th>$I_L$ [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(112)</td>
<td>(hhl)</td>
<td>39</td>
<td>40.708401</td>
<td>4.309290</td>
</tr>
<tr>
<td>(-1-1-2)</td>
<td>(hhl)</td>
<td>39</td>
<td>26.591999</td>
<td>2.814963</td>
</tr>
<tr>
<td>(11-2)</td>
<td>(hhl)</td>
<td>39</td>
<td>39.874802</td>
<td>4.221046</td>
</tr>
<tr>
<td>(-1-12)</td>
<td>(hhl)</td>
<td>39</td>
<td>47.053600</td>
<td>4.980977</td>
</tr>
<tr>
<td>(112)</td>
<td>(hhl)</td>
<td>0</td>
<td>54.132900</td>
<td>4.480233</td>
</tr>
<tr>
<td>(-1-12)</td>
<td>(hhl)</td>
<td>0</td>
<td>73.199600</td>
<td>6.058261</td>
</tr>
<tr>
<td>(11-2)</td>
<td>(hhl)</td>
<td>77</td>
<td>53.206799</td>
<td>4.403585</td>
</tr>
<tr>
<td>(-1-1-2)</td>
<td>(hhl)</td>
<td>77</td>
<td>56.057800</td>
<td>4.639545</td>
</tr>
<tr>
<td>(112)</td>
<td>(hhl)</td>
<td>13</td>
<td>62.961399</td>
<td>4.176178</td>
</tr>
<tr>
<td>(11-2)</td>
<td>(hhl)</td>
<td>90</td>
<td>70.618896</td>
<td>4.684094</td>
</tr>
<tr>
<td>(-1-12)</td>
<td>(hhl)</td>
<td>13</td>
<td>52.657799</td>
<td>3.492749</td>
</tr>
<tr>
<td>(-1-1-2)</td>
<td>(hhl)</td>
<td>90</td>
<td>58.328400</td>
<td>3.868875</td>
</tr>
</tbody>
</table>

#### Table A.8: Integrated intensities of symmetry equivalent reflexes of (121) at a Q position of 0.112 from $M_{IC}$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>plain</th>
<th>$\chi$ [°]</th>
<th>$I$ [a.u.]</th>
<th>$I_L$ [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(121)</td>
<td>(h2hl)</td>
<td>68</td>
<td>16.629101</td>
<td>1.869076</td>
</tr>
<tr>
<td>(-1-2-1)</td>
<td>(h2hl)</td>
<td>68</td>
<td>13.183700</td>
<td>1.481820</td>
</tr>
<tr>
<td>(12-1)</td>
<td>(h2hl)</td>
<td>68</td>
<td>24.212200</td>
<td>2.721400</td>
</tr>
<tr>
<td>(-1-21)</td>
<td>(h2hl)</td>
<td>68</td>
<td>22.759000</td>
<td>2.503764</td>
</tr>
<tr>
<td>(121)</td>
<td>(h2hl)</td>
<td>0</td>
<td>77.709198</td>
<td>3.255261</td>
</tr>
<tr>
<td>(12-1)</td>
<td>(h2hl)</td>
<td>43</td>
<td>72.662102</td>
<td>3.043836</td>
</tr>
<tr>
<td>(-1-21)</td>
<td>(h2hl)</td>
<td>0</td>
<td>70.117500</td>
<td>2.937242</td>
</tr>
<tr>
<td>(-1-2-1)</td>
<td>(h2hl)</td>
<td>43</td>
<td>72.432899</td>
<td>3.034235</td>
</tr>
</tbody>
</table>

#### Table A.9: Integrated intensities of symmetry equivalent reflexes of (200) at a Q position of 0.093 from $M_{IC}$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>plain</th>
<th>$\chi$ [°]</th>
<th>$I$ [a.u.]</th>
<th>$I_L$ [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(200)</td>
<td>(h0l)</td>
<td>90</td>
<td>74.667397</td>
<td>6.980267</td>
</tr>
<tr>
<td>(-200)</td>
<td>(h0l)</td>
<td>90</td>
<td>50.117699</td>
<td>4.685243</td>
</tr>
<tr>
<td>(200)</td>
<td>(h0l)</td>
<td>48</td>
<td>42.208900</td>
<td>2.934401</td>
</tr>
<tr>
<td>(-200)</td>
<td>(h0l)</td>
<td>48</td>
<td>3.742710</td>
<td>0.260197</td>
</tr>
<tr>
<td>(200)</td>
<td>(h0l)</td>
<td>48</td>
<td>114.821000</td>
<td>7.982461</td>
</tr>
<tr>
<td>(-200)</td>
<td>(h0l)</td>
<td>48</td>
<td>94.417503</td>
<td>6.563991</td>
</tr>
</tbody>
</table>
A.3 Appendix of chapter 7: Diffraction from a single mesocrystal

Table A.10: Integrated intensities of symmetry equivalent reflexes of (202) at a Q position of 0.125 from M\textsubscript{IC}. I are the uncorrected and I\textsubscript{L} are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

<table>
<thead>
<tr>
<th>hkl</th>
<th>plain</th>
<th>(\chi^\circ)</th>
<th>I [a.u.]</th>
<th>I\textsubscript{L} [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-202)</td>
<td>(h0l)</td>
<td>49</td>
<td>0.330552</td>
<td>0.041254</td>
</tr>
<tr>
<td>(20-2)</td>
<td>(h0l)</td>
<td>49</td>
<td>1.098830</td>
<td>0.137136</td>
</tr>
<tr>
<td>(202)</td>
<td>(h0l)</td>
<td>49</td>
<td>0.242135</td>
<td>0.030219</td>
</tr>
<tr>
<td>(-20-2)</td>
<td>(h0l)</td>
<td>49</td>
<td>-1.942690</td>
<td>-0.242451</td>
</tr>
</tbody>
</table>

Table A.11: Integrated intensities of symmetry equivalent reflexes of (220) at a Q position of 0.132 from M\textsubscript{IC}. I are the uncorrected and I\textsubscript{L} are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

<table>
<thead>
<tr>
<th>hkl</th>
<th>plain</th>
<th>(\chi^\circ)</th>
<th>I [a.u.]</th>
<th>I\textsubscript{L} [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220)</td>
<td>(hhl)</td>
<td>90</td>
<td>9.036520</td>
<td>1.194695</td>
</tr>
<tr>
<td>(-2-20)</td>
<td>(hhl)</td>
<td>90</td>
<td>-1.975710</td>
<td>-0.261204</td>
</tr>
</tbody>
</table>

Table A.12: Average of the integrated intensities of symmetry equivalent reflexes from M\textsubscript{IC}. \(\langle I_{exp}\rangle\) are the measured integrated intensities, Lorentz corrected and averaged and I\textsubscript{calc_rub} are the simulated intensities of the rounded cube model. Both are shown in figure 7.15b. R\textsubscript{int} and R\textsubscript{1} are the R factors known from crystallography, which quantify the quality of the data and the goodness of the fit, respectively. (R\textsubscript{1}-rounded cubes: 18%, R\textsubscript{1}-truncated cubes: 21%, R\textsubscript{1}-spheres: 13%)
Appendix A Additional Figures and Tables

(a) Truncated cubes model with $\tau_{\text{Trunc}} = 0$
  $a_{NP} = 8.27 \pm 0.0\%$, $a_{DW} = 0.501 \text{nm}$

(b) Truncated cubes model with $\tau_{\text{Trunc}} = 0.2$
  $a_{NP} = 8.4 \pm 0.0\%$, $a_{DW} = 0.84 \text{nm}$

(c) Truncated cubes model with $\tau_{\text{Trunc}} = 0.4$
  $a_{NP} = 8.38 \pm 0.1\%$, $a_{DW} = 0.594 \text{nm}$

(d) Truncated cubes model with $\tau_{\text{Trunc}} = 0.6$
  $a_{NP} = 8.59 \pm 0.6\%$, $a_{DW} = 0.744 \text{nm}$

(e) Truncated cubes model with $\tau_{\text{Trunc}} = 0.8$
  $a_{NP} = 8.69 \pm 3.8\%$, $a_{DW} = 0.00 \text{nm}$

(f) Truncated cubes model with $\tau_{\text{Trunc}} = 1.0$
  $a_{NP} = 9.64 \pm 6.1\%$, $a_{DW} = 1.29 \text{nm}$

Figure A.18: Results of fits from the truncated cube model. Figure A.18a fitted for a perfect cube and figure A.18f for a cubeoctaedron. The best parameters for the respective models are shown in figure A.18e.
A.3 Appendix of chapter 7: Diffraction from a single mesocrystal

(a) Rounded cubes model with $\tau_{\text{Round}} = 0$
$\alpha_{\text{NP}} = 8.197 \pm 0.0\%$, $\alpha_{\text{DW}} = 0.007 \text{ nm}$

(b) Rounded cubes model with $\tau_{\text{Round}} = 0.5$
$\alpha_{\text{NP}} = 8.714 \pm 1.2\%$, $\alpha_{\text{DW}} = 0.730 \text{ nm}$

(c) Rounded cubes model with $\tau_{\text{Round}} = 0.8$
$\alpha_{\text{NP}} = 10.42 \pm 0.0\%$, $\alpha_{\text{DW}} = 0.460 \text{ nm}$

(d) Rounded cubes model with $\tau_{\text{Round}} = 0.85$
$\alpha_{\text{NP}} = 10.78 \pm 0.4\%$, $\alpha_{\text{DW}} = 0.00 \text{ nm}$

(e) Rounded cubes model with $\tau_{\text{Round}} = 0.9$
$\alpha_{\text{NP}} = 11.21 \pm 0.0\%$, $\alpha_{\text{DW}} = 0.00 \text{ nm}$

(f) Rounded cubes model with $\tau_{\text{Round}} = 1.0$
$\alpha_{\text{NP}} = 12.01 \pm 0.0\%$, $\alpha_{\text{DW}} = 0.00 \text{ nm}$

Figure A.19: Results of fits from the rounded cube model. Figure A.19a fitted for a perfect cube and figure A.19f for a perfect spherical particle. The best parameters for the respective models are shown in figure A.19d.
Appendix B

Used algorithms

The following pages list the programs developed for this dissertation. These scripts were programmed in close collaboration with Artur Glavic. The author would appreciate that any publication resulting from using these scripts as basis would cite this source appropriately. The GISAXS framework Lógos from Artur Glavic and BornAgain written by Gennady Pospelov, Walter Van Herck, based on the model of chapter 5, are still under development and the results shown here only display the current snapshot.

B.1 Form factor fit for integrated intensities

```python
# <codecell>
from numpy import *
from ptylab import *
from matplotlib.colors import LogNorm, LinearSegmentedColormap

cmap=LinearSegmentedColormap.from_list('default', ['#0000ff', '#00ff00', '#ffffff', '#ff0000', '#ff00ff', '#000000'], N=256)

folder='/home/josten/mesotest_dr/

seterr(all='ignore')

def export_gnuplot(fname, *columns):
    output=open(fname, 'wb')
    if columns[0].ndim==1:
        data=array(columns)
        savetxt(output, data.transpose())
        output.close()
    else:
        data=array(columns)
        for i in range(columns[0].shape[1]):
            savetxt(output, data[:,i].transpose())
            output.write('
')
        output.close()

def lognorm(x,x0, sigma):
    return 1./(x*sigma*sqrt(2*pi))*exp(-0.5*(log(x)-log(x0))**2/sigma**2)

def ffc(Qx, Qy, Qz, a, tau):
    # set high precision complex numbers
    Qx=Qx.astype(complex128)
    Qy=Qy.astype(complex128)
    Qz=Qz.astype(complex128)
    a2=a/2.
    # truncated edge length is edge length times tau
    b=tau*a
    # Untruncated cubes form factor
    FC=a**3 * sinc(Qx*a2/pi) * sinc(Qy*a2/pi) * sinc(Qz*a2/pi)
```
Appendix B  Used algorithms

if tau != 0:
    # For the truncation calculate the scattering from all 8 edges
    # this is done by moving and rotating a quarter of an octahedron
    # as given in By R. W. HENDRICKS, J. SCHELLEN and W. SCHMA, Philosophical Magazine (1974)
    F8 = F0(Qx, Qy, Qz, b) * exp(-1j * a2 * (Qx + Qy + Qz))
    F8 += F0(-Qx, -Qy, -Qz, b) * exp(-1j * a2 * (-Qx - Qy - Qz))
    F8 += F0(-Qx, Qy, Qz, b) * exp(-1j * a2 * (-Qx + Qy + Qz))
    F8 += F0(Qx, -Qy, -Qz, b) * exp(-1j * a2 * (Qx - Qy - Qz))
    F8 += F0(Qx, -Qy, Qz, b) * exp(-1j * a2 * (Qx - Qy + Qz))
    F8 += F0(-Qx, Qy, -Qz, b) * exp(-1j * a2 * (-Qx + Qy - Qz))
    F8 += F0(Qx, Qy, -Qz, b) * exp(-1j * a2 * (Qx + Qy - Qz))
    return abs(FC - F8) ** 2
else:
    return abs(FC) ** 2

def F0(Qx, Qy, Qz, b):
    A = exp(1j * b * Qx) / (Qx * (Qx - Qy) * (Qx - Qz))
    B = exp(1j * b * Qy) / (Qy * (Qy - Qx) * (Qy - Qz))
    C = exp(1j * b * Qz) / (Qz * (Qz - Qx) * (Qz - Qy))
    D = 1.0 / (Qx * Qy * Qz)
    A[isnan(A.real) | isinf(A.real)] = 0j
    B[isnan(B.real) | isinf(B.real)] = 0j
    C[isnan(C.real) | isinf(C.real)] = 0j
    D[isnan(D.real) | isinf(D.real)] = 0j
    return 1j * (A + B + C - D)

def ffc_d(Qx, Qy, Qz, a, da, tau, steps=5):
    oshape = Qx.shape
    Qx = Qx.astype(complex128).flatten()
    Qy = Qy.astype(complex128).flatten()
    Qz = Qz.astype(complex128).flatten()
    delta = linspace(max(0, (1 - 2*da)), (1 + 2*da), steps)
    Pi = lognorm(delta, 1, da)
    Pi /= Pi.sum()
    a = a * delta[:, newaxis]
    Fd = ffc(Qx, Qy, Qz, a, tau)
    F = trapz(Pi[:, newaxis] * Fd, axis=0)
    return F.reshape(*oshape)

def ffs(Qr, r):
    QR = Qr * r
    return ((sin(QR) - QR * cos(QR)) / QR ** 3) ** 2

Qr = linspace(0, 1, 500).astype(complex128)
taus = linspace(0, 0.5, 100)

# <codecell>
figure(figsize=(13, 12))
res = []
for tau in taus:
    res.append(ffc(Qr, 0.0001*Qr, 0.0002*Qr, 50., tau))
res = array(res)
Q, T = meshgrid(Qr.real, taus)
pcolormesh(Q, T, res, norm=LogNorm(1e3, 1e10), cmap=cmap)
title('Truncation dependent cubes form factor in (H 0 0) direction for 5 nm cubes',
      fontsize=16)
xlabel('Q [AA$^{-1}$]', fontsize=16)
ylabel('nm', fontsize=16)
colorbar()
savefig(folder + '/single_meso_ff_H00.png', dpi=300)
# <codecell>
figure(figsize=(13, 12))
res = []
for tau in taus:
    res.append(ffc(sqrt(2) *Qr, sqrt(2.0001) * Qr, 0.0001*Qr, 50., tau))
res = array(res)
B.1 Form factor fit for integrated intensities

```python
Q,T = meshgrid(Qr.real, taus)
pcolormesh(Q,T,res, norm=LogNorm(1e3,1e10), cmap=cmap)
title('Truncation dependent cubes form factor in (H H 0) direction for 5 nm cubes', fontsize=16)
xlabel('Q [Å⁻¹]', fontsize=16)
ylabel('τ', fontsize=16)
colorbar()
savefig(folder+"/single_meso_ff_HH0.png", dpi=300)
```

```python
res=[]
for tau in taus:
    res.append(ffc(sqrt(3)*Qr, sqrt(3.0001)*Qr, sqrt(3.0002)*Qr, 50., tau))
res = array(res)
Q,T = meshgrid(Qr.real, taus)
pcolormesh(Q,T,res, norm=LogNorm(1e3,1e10), cmap=cmap)
title('Truncation dependent cubes form factor in (H H H) direction for 5 nm cubes', fontsize=16)
xlabel('Q [Å⁻¹]', fontsize=16)
ylabel('τ', fontsize=16)
colorbar();
savefig(folder+"/single_meso_ff_HHH.png", dpi=300)
```

```python
qx = linspace(0.00005,1.00005,200).astype(complex128)
qy = linspace(0.0001,1.0001,200).astype(complex128)
Qx,Qy = meshgrid(qx,qy)
Qz = Qx*1e-6
figure(figsize=(13,16))
for i, tau in enumerate([0, 0.1, 0.2, 0.3, 0.4, 0.5]):
    subplot('32 '+str(1+i))
    I=ffc(Qx, Qy, Qz, 50., tau)
xlim((-1,1.))
ylim((-1,1.))
pcolormesh(Qx.real,Qy.real,I, norm=LogNorm(1e3,1e10), cmap=cmap)
pcolormesh(-Qx.real,Qy.real,I, norm=LogNorm(1e3,1e10), cmap=cmap)
pcolormesh(Qx.real,-Qy.real,I, norm=LogNorm(1e3,1e10), cmap=cmap)
pcolormesh(-Qx.real,-Qy.real,I, norm=LogNorm(1e3,1e10), cmap=cmap)
title('τ=\%g' % tau)
xlabel('Qx [Å⁻¹]')
ylabel('Qy [Å⁻¹]')
colorbar();
export_gnuplot(folder+'/'+single_meso_ff_taus_%1f.dat %tau, Qx.real, Qy.real, I)
savefig(folder+"/single_meso_ff_taus.png", dpi=300)
```

```python
data = array([[1.0, 0.0, 1.0, 0.062400950016, 18.4212049128, 4.29199311658],
              [1.0, 1.0, 0.0, 0.0661037360179, 14.2881506228, 2.93087082572],
              [0.0, 0.0, 2.0, 0.105857500141, 4.34414952185, 0.758417415793],
              [2.0, 0.0, 0.0, 0.124801900032, -0.0590093060426, 0.161877029074],
              [2.0, 2.0, 0.0, 0.132207472036, 0.132207472036, 0.1],
              [0.0, 0.0, 4.0, 0.1653615, 1.2871956886, 0.228134450133]])
```

```python
astar = 0.0467424
```

# measured peaks as: H, K, L, |Q|, I, δI
```
Qz = L * cstar + 3e-6

Below the model and model function is defined, which is used to simulate the data.

Parameters are:

<table>
<thead>
<tr>
<th></th>
<th>Scaling intensity</th>
<th>Size of the cubes</th>
<th>truncation of the cubes</th>
<th>Debye–Waller displacement factor a</th>
</tr>
</thead>
<tbody>
<tr>
<td>I0</td>
<td>a</td>
<td>da</td>
<td>tau</td>
<td>dw_a</td>
</tr>
</tbody>
</table>

```python
from mpfit import mpfit
def f(p):
    I0 = p[0]
    a = p[1]
    da = p[2]
    tau = abs(p[3])
    dw_a = p[4]
    DW = exp(-1./3.* dw_a **2*(Qx **2+ Qy **2+ Qz **2))
    return I0 * ffc_d(Qx, Qy, Qz, a, da, tau)* DW

def residuals(p, fjac=None, use_error=True, use_log=False):
    if use_log:
        Iuse = maximum(I, 0.1*I[I>0].min())
        res = log(Iuse)-log(f(p))
        err = dI/Iuse
        else:
            res = (I-f(p))
            err = dI
        if use_error:
            return 0, res/err
        else:
            return 0, res

p0 = [9e-10, 85., 0.025, 0.5, 0.1] # 94., 0.05, 0.45, 5.]
```

# plot before fitting
errorbar(Q, I*Q**4, dI*Q **4)
plot(Q, f(p0)*Q**4)
plot(Q, 8e3 * ffs(Q, 59) *Q **4)
ylim((-1e-4, 1.2e-3))
xlabel('Q [Å⁻¹]')
ylabel('I*Q4');

# fit parameters
result = mpfit(residuals, p0, iterfunct=None)
p1 = result.params
result = mpfit(residuals, p0, functkw=dict(use_error=False), iterfunct=None)
p2 = result.params
result = mpfit(residuals, p0, functkw=dict(use_log=True), iterfunct=None)
p3 = result.params

# fit with different constant tau values
ptau = []
p0i = list(p0)
for tau in [0., 0.1, 0.2, 0.3, 0.4, 0.5]:
p0i = list(p0)
p0i[3] = tau
parinfo = [{ 'value': p0i[i], 'fixed':0, 'limited':[0,0], 'limits':[0,0.0]}
    for i in range(5)]
parinfo[2]['limited']=[True, True]
B.1 Form factor fit for integrated intensities

```python
parinfo[2]["limits"]=[0., 0.1]
parinfo[3]["fixed"] = True
parinfo[4]["limited"]=[True, True]
parinfo[4]["limits"]=[0., 20.]
for i in range(5): parinfo[i]["value"] = p0i[i]
result=mpfit(residuals, p0i, functkw=dict(use_log=False), iterfunct=None, parinfo=parinfo)
ptau.append(result.params)
p0i = result.params
print "I0=%.4g a=%.4g da=%.3g tau=%.4g dw_a=%.4g"%tuple(p0i)

# <code cell>
export_gnuplot(folder"/single_meso_refinement_result.dat", Q, I*Q**4, dI*Q**4, 
f(p1)*Q**4, f(p2)*Q**4, f(p3)*Q**4)

# <code cell>
Qr=np.linspace(0.05,0.18, 400)
def fcc_dw_rad(p, H, K, L):
    I0=p[0]
    a=p[1]
    da=abs(p[2])
    tau=abs(p[3])
    dw_a =p[4]
    DW =exp(-1./3.* dw_a **2*( Qr **2))
    uv_scale =sqrt((H*astar)**2+(K*astar)**2+(L*cstar)**2) # length of the unit vector in HKL direction
    Qx =Qr*H*astar/uv_scale +1e-6
    Qy =Qr*K*astar/uv_scale +2e-6
    Qz =Qr*L*cstar/uv_scale +3e-6
    return I0*ffcd(Qx, Qy, Qz, a, da, tau)*DW

def plot_all(ptaui, n, m, i, datfile=None):
    IH00=fcc_dw_rad(ptaui, 1, 0, 0)
    IH01=fcc_dw_rad(ptaui, 1, 1, 0)
    IH10=fcc_dw_rad(ptaui, 1, 0, 1)
    I2HHH=fcc_dw_rad(ptaui, 2, 1, 1)
    IHH2H=fcc_dw_rad(ptaui, 1, 1, 2)
    dw_a=ptaui[4]
    DW =exp(-1./3.* dw_a **2*( Qr **2))
    H00=[2,3,8]
    H01=[1,7]
    H10=[0,6]
    I2HHH=[5]
    HH2H=[4]
    IQ4=I*Q**4
dIQ4=d*Q**4
Qr=Q**4
if datfile is not None:
    export_gnuplot(datfile%ptaui[3], Qr, DW*0.001, IH00*Qr4, IH01*Qr4, IH10*Qr4, I2HHH*Qr4, HH2H*Qr4)

#figure(figsize=(8,6))
supplot(n=100*m+10+1)
errorbar(Q[H00], IQ4[H00], dIQ4[H00], fmt='.', color='red', label="Data", linewidth=2., markersize=10, capsize=5)
```

181
Appendix B  Used algorithms

```python
errorbar(Q[H0], IQ4[H0], dIQ4[H0], fmt='.', color='green', label=None,
        linewidth=2., markersize=10, capsize=5)
errorbar(Q[H0], IQ4[H0], dIQ4[H0], fmt='.', color='darkgreen', label=None,
        linewidth=2., markersize=10, capsize=5)
errorbar(Q[2HH], IQ4[2HH], dIQ4[2HH], fmt='.', color='blue', label=None,
        linewidth=2., markersize=10, capsize=5)
errorbar(Q[H2H], IQ4[H2H], dIQ4[H2H], fmt='.', color='darkblue', label=None,
        linewidth=2., markersize=10, capsize=5)
plot(Qr, DW *0.001, '-' , color='black', label="DW \cdot \frac{10^{-3}}{Q^4}", linewidth=2.)
plot(Qr, IH00 *Qr4, '-' , color='red', label="H00", linewidth=2.)
plot(Qr, IHH0 *Qr4, '-' , color='green', label="HH0", linewidth=2.)
plot(Qr, IH0H *Qr4, '--', color='darkgreen', label="H0H", linewidth=2.)
plot(Qr, I2HHH *Qr4, '-', color='blue', label="2HHH", linewidth=2.)
plot(Qr, IHH2H *Qr4, '--', color='darkblue', label="HH2H", linewidth=2.)
xlim((0.05, 0.18))
ylim((-1e-4, 1.2e-3))
legend(loc=2)
xlabel('Q [\AA]−1')
ylabel('I \cdot Q^4')
title('a =%.3f nm +/-%.1f%%
 tau =%.2f aDW =%.3f nm' % (ptaui[1]/10., abs(ptau[2])
                                    *100., ptaui[3], ptaui[4]/10.))

# export points with directional array
export_gnuplot(folder+'\single_meso_data.dat', Q, I, dI, I*Q**4, dI*Q**4, array
               ([3,2,1,1,5,4,3,2,1]))

# codecell >
figure(figsize=(13,16))
for i, ptaui in enumerate(ptau):
    plot_all(ptau, 3, 2, i+1, datfile=folder+'\single_meso_refinement_tau_%.1f.dat'
             )
savefig(folder+'\single_meso_refinement.png', dpi=300)
# markdowncell >
# Numeric form factor with FFT for rounded cubes
# codecell >
def normed_round_cube_realspace(tau, points, resolution):
a=1.
r=(a/2.*sqrt(3)-a/2.)*(1.-tau)+a/2.
x,y,z=mgrid[-a*resolution:points*1j,-a*resolution:points*1j,-a*resolution:points*1j]
dens=zeros_like(x)
dens[(abs(x)<=a/2.)&(abs(y)<=a/2.)&(abs(z)<=a/2.)]=1.
dens[(x**2+y**2+z**2)>r**2]=0
return dens
Is_tau={}
resolution=5

def getFFrcubes(qx, qy, qz, a, tau):
    if not tau in Is_tau:
        dens=normed_round_cube_realspace(tau, points, resolution):
    A=rfftn(dens)[:201,:201,:]
    I=abs(A**2)
    Is_tau[tau]=I
else:
    I=Is_tau[tau]
xsteps=2.*a*resolution/400.
qmax=pi/xsteps
qi=linspace(0., qmax, 201)
try:
    z=where(qi>abs(qx))[0][0]-1
    y=where(qi>abs(qy))[0][0]-1
    z=where(qi>abs(qz))[0][0]-1
```

182
except IndexError:
    # The Q value is out of the calculation range, return zero to prevent
    failure of fit
    return 1.e-300
qidx=(x,y,z)
Q=(qx, qy, qz)
w=[[1.,0.],[1.,0.],[1.,0.]]
Iout=0.
for i in range(3):
    if Q[i]!=qidx[i]:
        w[i][0]=1./(Q[i]-qi[qidx[i]])
        w[i][1]=1./(qi[qidx[i]]+1.-Q[i])
w[i][0]/=ws
w[i][1]/=ws
for i in range(2):
    for j in range(2):
        for k in range(2):
            Iout += w[0][i]*w[1][j]*w[2][k]*I[x+i,y+j,z+k]
return Iout

def FFrcubes(Qx, Qy, Qz, a, da, tau, steps=11):
    Iout=zeros(*Qx.shape, dtype=float)
    delta=linspace(max(0.,(1.-2*da)),(1.+2*da),steps)
P=lognorm(delta, 1., da)
P/=P.sum()
for di, Pi in zip(delta, P):
    ai =a*di
    for i in range(Qx.shape[0]):
        Iout[i]+=Pi*getFFrcubes(Qx[i], Qy[i], Qz[i], ai, tau)
    return Iout*30.

def f(p):
    I0=p[0]
    a=p[1]
    da=p[2]
    tau=abs(p[3])
    dw_a=p[4]
    DW=exp(-1./3.*dw_a**2*(Qx**2+Qy**2+Qz**2))
    return I0*FFrcubes(Qx, Qy, Qz, a, da, tau)*DW

p0r=[p0[0], 105., 0.025, 0.5, 0.1]
ptaur=[]
for tau in [0.,0.5, 0.8, 0.85, 0.9, 1.0]:
p0i=list(p0r)
p0i[3]=tau
parinfo = [{'value':0., 'fixed':0, 'limited':[0,0], 'limits':[0.,0.]}]
    for i in range(6):]
parinfo[3]["fixed"] = True
parinfo[1]["limited"]=[1,1]
parinfo[1]["limits"]=[65.]
parinfo[2]["limited"]=[65.]
parinfo[2]["limits"]=[0.1]
for i in range(6):
    parinfo[i]["value"]=p0i[i]
result=mpfit(residuals, p0i, functkw=dict(use_log=False), iterfunc=none, parinfo=parinfo)
ptaur.append(result.params)
p0i=result.params
print "I0=\%.4g a=\%.4g da=\%.3g tau=\%.4g du_a=\%.4g"%tuple(p0i)

# <codecell>
def fcc_dw_rad(p, H, K, L):
    I0=p[0]
    a=p[1]
    da=p[2]
    tau=abs(p[3])
    dw_a=p[4]
Appendix B Used algorithms

```python
448  DW = exp(-1.3 * dw_a ** 2 * (Qr ** 2))
449  uv_scale = sqrt((H * astar) ** 2 + (K * astar) ** 2 + (L * cstar) ** 2)  # length of the unit vector in HKL direction
450  Qx = Qr * H * astar / uv_scale
451  Qy = Qr * K * astar / uv_scale
452  Qz = Qr * L * cstar / uv_scale
453  return I0 * FFrcubes(Qx, Qy, Qz, a, da, tau) * DW
454
455  figure(figsize=(13, 16))
456  for i, ptau in enumerate(ptaur):
457      plot_all(ptau, 3, 2, i+1, datfile=folder + '/single_meso_refinement_rcubes_tau_%.2f.dat')
458      savefig(folder + '/single_meso_refinement_rcubes.png', dpi=300)
459      # <codecell>
460      IH00 = fcc_dw_rad(ptaur[5], 1, 0, 0)
461      IH0H = fcc_dw_rad(ptaur[5], 1, 0, 1)
462      I2HHH = fcc_dw_rad(ptaur[5], 2, 1, 1)
463      IHH2H = fcc_dw_rad(ptaur[5], 1, 1, 2)
464      dw_a = ptau[5][3]
465      DW = exp(-1./3.* dw_a ** 2 * (Qr ** 2))
466
467  xlim((0.05, 0.18))
468  ylim((-1e-4, 1.2e-3))
469  plot(Qr, 8.58 * ffs(Qr, 120.08/2.) * DW * Qr ** 4, '-', color='#aaaaaa', lw=10, label='Analytic Sphere')
470  plot(Qr, IH00 * DW * Qr ** 4, label='Numeric H00')
471  plot(Qr, IH0H * DW * Qr ** 4, label='Numeric H0H')
472  plot(Qr, I2HHH * DW * Qr ** 4, label='Numeric 2HHH')
473  plot(Qr, IHH2H * DW * Qr ** 4, label='Numeric HH2H')
474  legend()
475  savefig(folder + '/compare_rcubes_spheres.png', dpi=300)
476  # <codecell>
477  errorbar(Q, I * Q ** 4, dI * Q ** 4)
478  plot(Q, f(ptau[3]) * Q ** 4)
479  ylim((-1e-4, 1.2e-3))
480  xlabel('Q [Å]')
481  ylabel('I \cdot Q^4');
482  savefig(folder + '/single_meso_result_rcubes.png', dpi=300)
483  export_gnuplot(folder + '/single_meso_result_rcubes.dat', Q, I * Q ** 4, dI * Q ** 4, f(ptau[3]) * Q ** 4)
484
485  a = 107.7
486  x, y = mgrid[-resolution*a:resolution*a:400j, -resolution*a:resolution*a:400j]
487  figure(figsize=(11, 10))
488  dens = normed_round_cube_realspace(0.85, 400, resolution)
489  imshow(dens.sum(axis=2), cmap='gist_yarg', extent=[-resolution*a, resolution*a, -resolution*a, resolution*a])
490  xlim((-1.1*a, 1.1*a))
491  ylim((-1.1*a, 1.1*a))
492  xlabel('x [Å]')
493  ylabel('y [Å]')
494  savefig(folder + '/single_meso_realspace_projection_rcubes.png', dpi=300)
495  export_gnuplot(folder + '/single_meso_realspace_projection_rcubes.dat', x, y, dens.sum(axis=2))
496
497  figure(figsize=(11, 10))
498  imshow(dens[:,:,:200], cmap='gist_yarg', extent=[-resolution*a, resolution*a, -resolution*a, resolution*a])
499  xlim((-1.1*a, 1.1*a))
500  ylim((-1.1*a, 1.1*a))
501  xlabel('x [Å]')
502  ylabel('y [Å]')
503  savefig(folder + '/single_meso_realspace_shadow_rcubes.png', dpi=300)
```

184
B.1 Form factor fit for integrated intensities

```python
export_gnuplot(folder+"/single_meso_realspace_shadow_rcubes.dat", x, y, dens[:, :, 200])
del(dens)

# Implementation of radial integrated form factor for SAXS refinement

def FFrSAXS(Qr, a, da, tau):
    if not tau in Is_tau:
        dens = normed_round_cube_realspace(tau, 400, resolution)
        A = rfftn(dens)
        I = abs(A ** 2)
        Is_tau[tau] = I
    else:
        I = Is_tau[tau]
    # calculate Q-vectors normalized by a
    xsteps = 2. * resolution / 400.
    steps = 200
    Qmax = pi / xsteps
    Qx, Qy, Qz = mgrid[0: Qmax: steps * 1j, 0: Qmax: steps * 1j, 0: Qmax: steps * 1j]
    Qr_a = sqrt(Qx ** 2 + Qy ** 2 + Qz ** 2)
    Qr_high = Qr_a / maximum(1e-10, a - 3. * da * a)
    Qr_low = Qr_a / (a + 3. * da * a)
    Iout = zeros_like(Qr)
    for i, Qri in enumerate(Qr):
        region = where((Qr_low <= Qri) & (Qr_high > Qri))
        weights = lognorm(Qr_a[region] / Qri, a, da)
        Iout[i] = (I[region] * weights).sum() / weights.sum()
    return Iout
```

```python
Qr = linspace(0., 0.3, 200)
result = [FFrSAXS(Qr, 100., 0.05, 0.85), FFrSAXS(Qr, 100., 0.05, 0.50),
          FFrSAXS(Qr, 100., 0.10, 0.85), FFrSAXS(Qr, 100., 0.20, 0.85)]
export_gnuplot(folder+"/single_meso_rcubes_ff.dat", Qr, *result)
semilogy(Qr, result[0], label="tau = 0.85 sigmaa = 0.05")
semilogy(Qr, result[1], label="tau = 0.50 sigmaa = 0.05")
semilogy(Qr, result[2], label="tau = 0.85 sigmaa = 0.10")
semilogy(Qr, result[3], label="tau = 0.85 sigmaa = 0.20")
legend()
xlabel('Q [Å⁻¹]')
ylabel('I')
title('Radial integrated form factor of rounded cubes')
savefig(folder+"/single_meso_rcubes_ff.png", dpi=300);
```

# Load the SAXS data and fit the form factor with tau=0.85.

```python
data = loadtxt('saxsdata.dat')
Qr = data[:, -1, 0]
Ir = data[:, -1, 1]
dIr = data[:, -1, 2]
fitregion = where(Ir > 0.)[0][50: -20]
```

# Residuals used for SAXS refinement

```python
def resSAXS(p, fjac=None):
    I0 = p[0]
    a = p[1]
    da = p[2]
    tau = p[3]
    BG = p[4]
    sigmaQ = p[5]
```

185
Appendix B  Used algorithms

res = np.exp(-0.5*(Qr - Qr.mean())**2/sigmaQ**2)
res /= res.sum()
I = I0*FFrSAXS(Qr, a, da, tau) + BG
I = convolve(I, res, mode='same')[fitregion]
err = dIr[fitregion]/Ir[fitregion]
return 0, (log(I[fitregion]) - log(I))/err

pSAXS = [4.50215333e-09, 1.09122571e+02, 0.05067, 0.85, 0.00101633, 0.00379122]
parinfo = [{'value':0., 'fixed':0, 'limited':[0.,0.], 'limits':[0.,0.]}]
for i in range(6):
    parinfo[i]['fixed'] = True
for i in range(6):
    parinfo[i]['value'] = pSAXS[i]
result = mpfit(resSAXS, pSAXS, parinfo=parinfo, maxiter=10, iterfunct=None)

def Isim(p):
    I0 = p[0]
a = p[1]
da = p[2]
tau = p[3]
BG = p[4]
sigmaQ = p[5]
res = np.exp(-0.5*(Qr - Qr.mean())**2/sigmaQ**2)
res /= res.sum()
I = I0*FFrSAXS(Qr, a, da, tau) + BG
I = convolve(I, res, mode='same')[fitregion]
return I

ISAXSSim = Isim(result.params)

# <codecell>
figure(figsize=(12,10))
semilogy(Qr, Ir, label='data')
export_gnuplot(folder+'/single_meso_rcubes_ff_fit.dat', Qr, Ir, ISAXSSim)
semilogy(Qr, ISAXSSim, label='fit')
legend()
xlabel('Q [Å⁻¹]')
ylabel('I')
title('SAXS fit of rounded cubes')
savefig(folder+'/single_meso_rcubes_ff_fit.png', dpi=300);

# <codecell>
p0SAXS = result.params
pSAXStau = []
for tau in [0.85, 0.825, 0.8, 0.775, 0.75]:
pSAXS = list(p0SAXS)
pSAXS[3] = tau
parinfo = [{'value':0., 'fixed':0, 'limited':[0.,0.], 'limits':[0.,0.]}]
for i in range(6):
    parinfo[i]['fixed'] = True
    parinfo[i]['value'] = pSAXS[i]
result = mpfit(resSAXS, pSAXS, iterfunct=None, maxiter=5, parinfo=parinfo)
pSAXStau.append(result.params)
print tau, result.fnorm

# <codecell>
p0i = [9e-10, 108.99, 0.058, 0.8, 0.04]
parinfo = [{'value':0., 'fixed':0, 'limited':[0.,0.], 'limits':[0.,0.]}]
for i in range(5):
    parinfo[i]['fixed'] = True
parinfo[1]['fixed'] = True
parinfo[2]['fixed'] = True
B.2 Laue function fit for single mesocrystal

```python
parinfo[3]["fixed"] = True
for i in range(5): parinfo[i]["value"] = p0i[i]
result = mpfit(residuals, p0i, functkw=dict(use_log=False), iterfunct=None, parinfo=parinfo)
result.params
plot_all(result.params, 2, 2, 1, datfile=folder + '/single_meso_refinement_rcubes_SAXSfit_tau_%.2f.dat')
plot_all(ptaur[3], 2, 2, 2)

subplot(223)
errorbar(Q, I*Q**4, dI*Q**4)
plot(Q, f(result.params)*Q**4)
ylim((-1e-4, 1.2e-3))
xlabel('Q [Å⁻¹]');
ylabel('I\cdot Q^4');

subplot(224)
errorbar(Q, I*Q**4, dI*Q**4)
plot(Q, f(ptaur[3])*Q**4)
ylim((-1e-4, 1.2e-3))
xlabel('Q [Å⁻¹]');
ylabel('I\cdot Q^4');

export_gnuplot(folder + '/single_meso_result_rcubes_after.dat', Q, I*Q**4, dI*Q**4, f(result.params)*Q**4)
savefig(folder + '/single_meso_result_rcubes_after.png', dpi=300)
```

---

B.2 Laue function fit for single mesocrystal

```python
from numpy import sqrt, sin, cos, arange, exp, newaxis, pi, linspace, zeros_like
class SpheresLaue(fit_data.FitFunction):
    name = "Spheric FF+Laue"
    parameters = [1., 100., 0.01, 0., 150., 0., 20., 2.01]
    parameter_names = ['I', 'r', '\delta r', 'Qx', 'c', '\delta c', 'N', '\delta N', 'Inc']
    parameter_description = {'I': 'Scaling', 'r': 'Particle Radius', 'Qx': 'Q-offset'}
    fit_function_text = 'Moved Laue Function'

    def fit_function(self, p, x):
        I0, r, dr, Qx = p[0:4]
        c, dc, N, dN = p[4:8]
        Inc = p[8]
        R = linspace(r*(1.-3*dr), r*(1+3*dr), 20)
        Pr = exp(-0.5*(R-r)**2/(r*dr)**2)
        Pr /= Pr.sum()
        Qr = sqrt(Qx**2 + x**2)*R[ newaxis , :]
        FF = I0*(Pr[ newaxis , :]*((sin(Qr)-Qr*cos(Qr))**2/Qr**6)).sum(axis=1)
        L = zeros_like(x)
        scales = linspace(1-3*dc, 1+3*dc, 21)
        P = exp(-0.5*((scales-1)/dc)**2)
        P /= P.sum()
        for Pi, scale in zip(P, scales):
            Ql = x*c/2*scale
            L += self.laue(Ql, N, dN)
        return FF*(L+Inc)

    def laue(self, Ql, N, dN):
        if dN > 0:
            Nmin = min(int(N)-3, int(N-3*dN))
            Nmax = max(int(N)+3, int(N+3*dN))
            n = arange(Nmin, Nmax+1)
            P = exp(-0.5*((n-N)/dN)**2)
            P /= P.sum()
```

---
Appendix B  Used algorithms

```python
Laue = abs((exp(1j*(Ql+pi))+1.)[:,newaxis]*sin(Ql[:,newaxis]*n[newaxis,:])/sin(Ql[:,newaxis]))**2
L=(Laue*P[newaxis,:]).sum(axis=1)
else:
L=abs((exp(1j*(Ql+pi))+1.)*sin(Ql*int(N))/sin(Ql))**2
return L
```

B.3 Single mesocrystal modeling

```python
# <codecell>
from numpy import *
from scipy.special import j1
from scipy.signal import fftconvolve
from pylab import *
from matplotlib.colors import LogNorm, LinearSegmentedColormap
import matplotlib

folder='/home/josten/mesotest/

# nstar=2.*pi/235.
# cstar=2.*pi/280.
astar=0.046645771
cstar=0.041500563

h_MC=2150.
r_MC=22000.
DW_MC=5.
def F_MC(Qy, Qz):
    F=sinc(h_MC*Qz/pi)
    F[Qy!=0]*=j1(r_MC*Qy[Qy!=0])/(r_MC*Qy[Qy!=0])
    return F

r_NP=58.0
def F_NP(Q, r):
    Qr=Q*r
    return (sin(Qr)-Qr*cos(Qr))/Qr**3

# <codecell>
qy=linspace(-0.01,0.01,400)
qz=linspace(-0.01,0.01,400)
Qy,Qz=meshgrid(qy,qz)

I=abs(F_MC(Qy,Qz)**2)
figure(figsize=[14,10])
gca().set_xlim([-0.01,0.01])
gca().set_ylim([-0.01,0.01])
pcolormesh(Qy,Qz,1, norm=LogNorm(1e-7,1))
colorbar()
savefig(folder+'single_meso_simu_peakshape.png', dpi=300);

# <codecell>
qy=linspace(-0.01,0.21,2200)
qz=linspace(-0.01,0.21,2200)
Qy,Qz=meshgrid(qy,qz)
A=zeros_like(Qy)
for H in range(-1,6):
    for L in range(-1,6):
        if (H+L)%2==1:
            continue
```

fit_data.FitSession.available_functions_2d[SpheresLaue.name]=SpheresLaue
B.3 Single mesocrystal modeling

\[ A = F_{MC}(Qy - H \astar, Qz - L \cstar) \]

\[ |H0L| = \text{abs}(A^2) \]

```python
# <code cell>
A = zeros_like(Qy)
for HK in range(-1,3):
    for L in range(0,6,2):
        A+= F_MC(Qy-HK*sqrt(2.)*astar,Qz-L*cstar)

IH0L = abs(A**2)
# <code cell>
sigmax = 0.00031
sigmay = 0.00031
res = exp(-0.5*((Qy-qy.mean())/(sigmax)**2+((Qz-qz.mean())/(sigmay)**2))
res /= res.sum()
IH0L_res = fftconvolve(res, IH0L, mode="same")
IH0L_res = fftconvolve(res, IHHL, mode="same")
# <code cell>
sigma_r = 0.1
ri = linspace(-3*sigma_r,3*sigma_r,11)+r_NP
Pi = exp(-0.5*((r_NP-ri)**2/sigma_r**2)
Pi /= Pi.sum()
FF = zeros_like(Qy)
Qr = sqrt((Qy**2+Qz**2))
for rii, Pii in zip(ri, Pi):
    FF += Pii * F_NP(Qr, rii)**2
# <code cell>
DW = exp(-1./3.*DW_MC**2*(Qy**2+Qz**2))
# <code cell>
cmap = LinearSegmentedColormap.from_list('default', ['#0000ff', '#00ff00', '#ffffff', '#ff00ff', '#0000ff'], N=256)
L = 4e-4*minimum(1e4, array([1./(Qz-0.11)**2, 1./(Qz-0.055)**2, 1./Qz**2, 1./(Qz +0.055)**2, 1./(Qz-0.11)**2]).max(axis=0))*minimum(1e3, 1./Qy**2)
C = 500.
figure(figsize=[13,12])
imshow(((L*IH0L_res*DW+1e-3)*FF)*((Qy**2+Qz**2) >0.0008), cmap=cmap, norm=LogNorm(6e-6, 6e-2),
extent=[qy.min(), qy.max(), Qz.max(), qz.min()])
title('H0L - Plane')
xlabel('Qy')
ylabel('Qz')
colorbar()
savefig(folder+'single_meso_simu_H0L.png', dpi=300);
# <code cell>
figure(figsize=[13,12])
imshow(((L*IHHL_res*DW+1e-3)*FF)*((Qy**2+Qz**2) >0.0008), cmap=cmap, norm=LogNorm(1e-5, 3e-2),
extent=[qy.min(), qy.max(), Qz.max(), qz.min()])
title('HHL - Plane')
xlabel('Qy')
ylabel('Qz')
colorbar()
savefig(folder+'single_meso_simu_HHL.png', dpi=300);
# <code cell>
```
Appendix B  Used algorithms

# export data

def export_gnuplot(fname, x, y, z):
    output = open(fname, 'wb')
    data = array([x, y, z])
    for i in range(Qy.shape[1]):
        savetxt(output, data[:, i], transpose())
    output.write('
')
    output.close()

export_gnuplot(folder + 'single_meso_simu_H0L.dat',
                Qy, Qz, ((C* IH0L_res *DW +1e-3) *FF) *((Qy**2+Qz**2)>0.0008))
export_gnuplot(folder + 'single_meso_simu_HHL.dat',
                Qy, Qz, ((C* IHHL_res *DW +1e-3) *FF) *((Qy**2+Qz**2)>0.0008))
export_gnuplot(folder + 'single_meso_simu_H0L_Lorentz.dat',
                Qy, Qz, ((L* IH0L_res *DW +1e-3) *FF) *((Qy**2+Qz**2)>0.0008))
export_gnuplot(folder + 'single_meso_simu_HHL_Lorentz.dat',
                Qy, Qz, ((L* IHHL_res *DW +1e-3) *FF) *((Qy**2+Qz**2)>0.0008))

# <codecell>

B.4 Peak shape computation for in-situ experiments

```
# coding: utf-8

'''
Load a set of measurements and fit a peak function for each dataset.
'''

import os, sys
import shutil
import time
from glob import glob
from copy import deepcopy
from plot_script.read_data.kws2 import read_edf_file
from form_factors import FitSphereQres
from neue_funktion_final import PeakShapeResTilt

stdout = None

print "Usage:
-Open one dataset and make your correction:
d=filter_dataset(dataset(), [0.,10.,0.,10.])
  session.active_file_data.append(d)
  remove_bg(d)
  remove_sphere(d)
  # <ctrl>+N

-Run the fits for all files in the active directory:
z.B. plots_for_all(preset='s113')
  plots_for_all(fit_function=None,
                name='Fits',
                store_data=False,
                correction=None,
                remove_background=False,
                preset=None)"

SPHERE_PARAMS=[
    0.000577067, # I 0
    0., # BG
    50.0518, # R
    0.0638503, # \delta R
    0.0035, # \Delta \Theta vorher
    1e-10, # \Delta
    4.51, # \lambda
]
```
B.4 Peak shape computation for in-situ experiments

CUBES_PARAMS =
[0.000577067, # I0
 0.056517, # SR
 0.0035, # ΔΘ
 1e-10, # Δ
 4.51, # λ
]

# x-from x-to y-from y-to
BG_REGION = [0.15, 0.16, 0.21, 0.229] # vorher
PG_REGION = [0.151, 0.161, 0.22, 0.229] # P321, P227

def iteration_update(step_add=None, info=' '):
  '''
  Define a function which updates the user on the current fit iteration.
  '''
  stdout.write(info +'
')
  stdout.flush()
  return 0

def fit_data_list(datasets, # list of file names
  initial_fit=None, # Fit function to be used, if None uses fit-0
  from active dataset
  correction=None, # form factor correction function to be used
  remove_background=False, # remove the background
  plot_prefix='Result', # name of session.file_data list to append
datasets to
  incregion=None, # region to extract incoherent scattering
  ii_region=None, # region to calculate integrated intensity
  param_file=None, # file to store the text data to
)

  '''
  Starting from a given fit (if None uses the first
  fit of the active dataset) all datasets in a list of
  names are read and fit. The result parameters for each
  file are returned as a list.
  '''
  global stdout, do_plot
  if stdout is None:
    try:
      stdout = plot_gui.status_dialog
      do_plot = True
    except:
      stdout = sys.stdout
      do_plot = False
  from config import gnuplot_preferences
  gnuplot_preferences.settings_3dmap += 'set format cb "10^{%L}"
    set cblabel offset 1.5
  
  gnuplot_preferences.plotting_parameters_3d = 'w points palette ps .1 pt 5'
  if do_plot:
    import gtk
    keep_running = gtk.CheckButton(label='Keep Running')
    keep_running.set_active(True)
    stdout.vbox.pack_end(keep_running, False)
    keep_running.show()
    stdout.present()
  if initial_fit is None:
    # get first fit from active dataset
    fit = dataset().fit_object.functions[0][0]
  else:
    fit = initial_fit
# create multiprocessing framework
fit.activate_multiprocessing()

if param_file is not None:
    param_file = open(param_file + '.txt', 'w')
    param_file.write("\t".join(fit.parameter_names)+"\n"
    "\t".join(["\t"+name for name in fit.parameter_names])+
    "\t# Time\n")
    param_file.flush()

parameters = []
ff = None  # form factor intensity array
incidxs = None
ii_idx = None
first_time = None

for i, ds in enumerate(datasets):
    stdout.write(" Reading %s ...
" % ds)
    stdout.flush()
    # read dataset and extract number and time
    data = read_edf_file(ds)[0]
    info = map(lambda line: map(str.strip, line.split(':')), data.info.splitlines())
    info = dict(filter(lambda item: len(item) == 2, info))
    file_number = int(ds.rsplit('_', 1)[1].split('ccd')[0])
    gmtime = time.strptime(info['HMStartTime'].split('.')[0], '%Y-%m-%dT%H:%M:%S')
    float_time = time.mktime(gmtime)
    if remove_background:
        stdout.write(" ... background ...
")
        stdout.flush()
        remove_bg(data)
    if correction is not None:
        stdout.write(" ... correcting ...
")
        stdout.flush()
    # filter the dataset for the fitted region
    dataf = filter_dataset_fitregion(data, fit)
    # clear all references to the data and delete the temporary file
    data.store_data()
    os.remove(data.tmp_export_file)
    del(data)
    data = dataf
    if ff is None:
        # calculate the form factor correction intensities on first call
        ff = correction(data)
        data.z /= ff
    if incregion is not None:
        stdout.write(" ... incoherent background ...
")
        stdout.flush()
        if incidxs is None:
            incidxs = np.where((data.x >= incregion[0]) & (data.x <= incregion[1]) &
                                (data.y >= incregion[2]) & (data.y <= incregion[3]))
            incdata = float(data.z[incidxs].sum()) / len(data.z[incidxs])
        bg_param_index = fit.parameter_names.index('BG
')
        fit.parameters[bg_param_index] = incdata
        if bg_param_index in fit.refine_parameters:
            fit.refine_parameters.remove(bg_param_index)
        stdout.write(" ... %g ...
" % incdata)
        stdout.flush()
    if ii_region is not None:
        stdout.write(" ... integrated intensity ...
")
        stdout.flush()
        if ii_idx is None:
            ii_idx = np.where((data.x >= ii_region[0]) & (data.x <= ii_region[1]) &
                                (data.y >= ii_region[2]) & (data.y <= ii_region[3]))
            ii_data = data.z[ii_idx].sum() / len(data.z[ii_idx])
        if incregion is not None:
            ii_data -= incdata
        stdout.write(" %f
" % (float(ii_data)))
        stdout.flush()
B.4 Peak shape computation for in-situ experiments

```python
stdout.write("... refining ...
")
stdout.flush()
fitmsg, covar = fit.refine(data.x, data.y, data.z, None, # data.z.error, # None =
    ignore errors, data.z.error=\bercksichtigung
    progress_bar_update=iteration_update) # Fit Routine

errors=[]
if fitmsg!='':
    stdout.write("Error in Fit: "+fitmsg)
    stdout.flush()
errors=[np.sqrt(covar[i][i]) for i in range(len(fit.parameters))]
if first_time is None:
    first_time=float_time
float_time-=first_time
if ii_region is None:
    fit_parameters=list(fit.parameters)+errors+[file_number, float_time]
else:
    fit_parameters=list(fit.parameters)+[float(ii_data.data.error)]+
    errors+[float(ii_data.data.error)],[file_number, float_time]
parameters.append(fit_parameters)
if param_file is not None:
    param_file.write("\t".
    join(["%g"%param for param in fit_parameters])"
    param_file.flush()

stdout.write("... result:
\t%s
\t%s
+/ -	%s

"% (repr(fit.parameter_names),
repr(fit.parameters),
repr(errors)))
```

# create fit data for plotting
data.is_matrix_data=False
data.plot_options.xrange=[fit.x_from,fit.x_to]
data.plot_options.yrange=[fit.y_from,fit.y_to]
data.plot_options.zrange=[1.,1000.]
data.plot_together_zindex=-1
fit_data=mds.MeasurementData([],x=0,y=1,zdata=2)
fit_data.data.append(data.x)
fit_data.data.append(data.y)
fit_data.data.append(mds.PhysicalProperty(data.z.dimension, data.z.unit,
    fit(data.x, data.y)))
data.plot_together.append(fit_data)
data.sample_name=''
data.short_info='#%i' % file_number
session.picture_width='2400'
session.picture_height='1200'
if do_plot:
    # plot an image and copy the result
    plot_gui.measurement[0]=data
    replot()
    shutil.copy(session.TEMP_DIR+’/plot_temp.png’, plot_prefix+’%04i.png’%file_number)
else:
    # directly plot as file
    mdp.gnuplot_plot_script(session,
        [data],
        ’temp_plot’,
        ’.png’,
        data.short_info,
        [data.short_info],
        False,
        plot_prefix+’%04i.png’%file_number)
# clear all references to the data and delete the temporary file
data.store_data()
for file in data:
    del(file)
if do_plot and not keep_running.get_active():
    # stop iteration due to user input
    break
# terminate other processes
fit.deactivate_multiprocessing()
if do_plot:
    stdout.vbox.remove(keep_running)
```
Appendix B  Used algorithms

```python
return np.array(parameters).transpose()

def plots_from_paramlist(parameters, parameter_names):
    # create plots of parameters
    idx = mds.PhysicalProperty('File No.', '', parameters[-2])
    tm = mds.PhysicalProperty('Time', 's', parameters[-1])
    for i, name in enumerate(parameter_names):
        ds = mds.MeasurementData(x=0, y=2)
        ds.data.append(tm)
        ds.data.append(idx)
        if np.all(parameters[len(parameter_names)+i] == 0):
            ycol = mds.PhysicalProperty(name, '', parameters[i])
        else:
            ycol = mds.PhysicalProperty(name, '', parameters[i],
                                         parameters[len(parameter_names)+i])
        ds.data.append(ycol)
        session.active_file_data.append(ds)

def plots_for_all(fit_function=None, name='Fits',
                  store_data=True, correction=None, remove_background=False,
                  param_file=None, preset=None):
    '''
    Perform analysis for all files in the active directory
    starting from the last file. Options can be given
    when called or using the preset name.
    '''
    global params, initial_fit
    files = glob('*. edf')
    files.sort()
    files.reverse()
    if preset is None:
        initial_fit = None
        incregion = None
        ii_region = None
    else:
        preset = fit_presets[preset]
        initial_fit = PeakShapeResTilt(list(preset['initial_fit']))
        initial_fit.use_rotation = preset['use_rotation']
        min_x = 1000.
        max_x = -1000.
        min_y = 1000.
        max_y = -1000.
        initial_fit.refine_parameters = range(8)+[13, 14]  # all free peak parameters +
        background and αc
        initial_fit.regions = []
        for xf, xt, yf, yt, Ii, Qyi, Qzi in preset['peaks']:
            # set the fit region as maximum from all peak ranges
            min_x = min(min_x, xf)
            max_x = max(max_x, xt)
            min_y = min(min_y, yf)
            max_y = max(max_y, yt)
            # add the peak to the fit function
            i = len(initial_fit.regions)
            initial_fit.add_region(xf, xt, yf, yt, Ii, Qyi, Qzi)
            # if i in [0]:
            #    initial_fit.refine_parameters += [15+3*i] # free intensity
            # else:
            #    initial_fit.refine_parameters += [15+3*i, 17+3*i] # free intensity and Qz
            # constrain intensities to be >= 0
            initial_fit.constrains[14] = ('bounds': [0., None], 'tied': '') # αc>=0
            for i in range(len(initial_fit.regions)):
                if (15+3*i) in initial_fit.constrains:
                    initial_fit.constrains[15+3*i][0] = 0.
            else:
                initial_fit.constrains[15+3*i] = ('bounds': [0., None], 'tied': '')
            initial_fit.x_from = min_x
            initial_fit.x_to = max_x
```
B.4 Peak shape computation for in-situ experiments

```python
initial_fit.y_from = min_y
initial_fit.y_to = max_y
if preset['mirror_peaks']:
    initial_fit.add_mirrors()
correction = preset['correction']
remove_background = preset['remove_background']
increment = preset['increment']
ii_region = preset['ii_region']
if param_file is None:
    param_file = preset['param_file']
if name == 'Fits':
    name = preset['name']
# fit all datasets
params = fit_data_list(files,
correction=correction,
remove_background=remove_background,
initial_fit=initial_fit,
plot_prefix=param_file+'_',
ii_region=ii_region,
increment=increment,
param_file=param_file)
# if param_file is not None:
# params[-1]=params[-1].min()
# np.savetxt(param_file+'-1.txt', params.transpose(), fmt='%12g', delimiter='\t')
# create plots for parameters
session.file_data[name]=[]
session.active_file_data = session.file_data[name]
session.active_file_name = name
plots_from_paramlist(params, initial_fit.parameter_names)
try:
    plot_gui.rebuild_menus()
    replot()
except:
    pass

def remove_sphere(ds):
    '''
    Divide the measured intensity by the particle formfactor.
    '''
    ff=ff_sphere(ds)
    ds.z/=ff

def ff_sphere(ds):
    # sphere form factor
    FF=FitSphereQres(SPHERE_PARAMS)
    return FF(np.sqrt(ds.x**2+ds.y**2))

def remove_cube(ds):
    '''
    Divide the measured intensity by the particle formfactor.
    '''
    ff=ff_cube(ds)
    ds.z/=ff

def ff_cube(ds):
    # cube form factor
    FF=FitSphereQres(CUBES_PARAMS)
    return FF(np.sqrt(ds.x**2+ds.y**2))

def remove_bg(ds):
    '''
    Subtract background.
    '''
    bg=BG_REGION
    bg=ds.z[(ds.x>=rg[0])&(ds.x<=rg[1])&
             (ds.y>=rg[2])&(ds.y<=rg[3])]
    bg=bg.sum()/len(bg)
    ds.z-=bg #P231, P227
```
Appendix B  Used algorithms

```python
# def filter_dataset(ds, region):
#   '''
#   Get a new dataset for a region defined by [x0, x1, y0, y1]
#   '''
#   ids = np.where((ds.x >= region[0]) & (ds.x <= region[1]) &
#                  (ds.y >= region[2]) & (ds.y <= region[3]))
#   return ds[ids]

def filter_dataset_fitregion(ds, fit):
    '''
    Get a new dataset for a region defined by PeakShapeResTilt peak regions.
    '''
    ids = ds.x != ds.x  # all False
    for region in fit.regions:
        ids = ids | ((ds.x >= region[0]) & (ds.x <= region[1]) & (ds.y >= region[2]) & (ds.y <= region[3]))
    return ds[ids]

# Parameters for different Peaks
fit_presets={
    'P231ai03': {
        'initial_fit': [  # General peak parameters
            # 'a', 'c', y', y'z'
            0.058643, 0.0208204, 0.000276603, 0.000432451,
            # 'tilt', c'
            4.92985, 0.0179373,
            # 'Qy_off', 'Qz_off', 'Qphi_off' is fixed
            -0.00219964, 0.00659495, -0.577801,
            # 'width', 'height', 'decay' is fixed
            0.00497968, 0.000754677, 3195.79,
            # 'a', 'c'
            0.3, 0.0000244498,
            # BG
            27,
        ],
        'peaks': [  # parameters for each single peak
            # xfrom, xto, yfrom, yto, I, H/K/L
            [0.026, 0.09, 0.154, 0.185, 5e5, 1, 0], # 108
            [0.026, 0.087, 0.073, 0.11, 5e5, 1, 4], # 104
            [0.026, 0.087, 0.089, 0.127, 5e5, 1, 6], # 105
            [0.07, 0.116, 0.049, 0.088199, 5e5, np.sqrt(3.), 3], # 113
            [0.09, 0.14, 0.067, 0.107, 5e5, 2, 4], # 204
            [0.07, 0.116, 0.10465835093, 0.146, 5e5, np.sqrt(3.), 6] # 116
        ],
        'mirror_peaks': True,  # add peaks from the left side
        'use_rotation': True,
        'correction': 'ff_sphere',
        'remove_background': True,
        'param_file': 'P231_Spheres_short_ai03_timedependence_final',
        'name': 'P231_Spheres_short_ai03',
        'int_region': [0.035, 0.08, 0.096, 0.13],  # Integrated intensity around 0.15
        'inregion': [0.02, 0.03, 0.095, 0.11],
    },

    'P226ai03': {
        'initial_fit': [  # General peak parameters
            # 'a', 'c', y', y'z'
            0.056734, 0.0200253, 0.0000322504, 0.000158157,
            # 'tilt', c'
            2.73872, 0.0162109,
            # 'Qy_off', 'Qz_off', 'Qphi_off' is fixed
            -0.00189297, 0.00698159, -0.564942,
            # 'width', 'height', 'decay' is fixed
            0.00497968, 0.000754677, 3195.79,
            # 'a', 'c'
        ]
    }
```
B.4 Peak shape computation for in-situ experiments

```python
import numpy as np
from scipy.signal import fftconvolve
from plot_script.fit_data import FitFunction3D, register_class
from multiprocessing import Pool

LAMBDA = 4.51  # Å

class PeakShapeResTilt(FitFunction3D):
    """Fit a Gaussian or Lorentzian peak function with radial tilting distribution
    and a beam shape function convoluted with fft.
    ""
    # define class variables
    name = "Mesopeak + Resolution"
    # default parameters
    parameters = [0.068, 0.021, 0.0001, 0.0001, 0.0, 0.001, 0.0, 0.0, 0.0, 0.0, 0.00531166, 0.000941805, 9233.57, 0.3, 0.1, 0.0, 0.0, 0.0]
    # names of parameters
    parameter_names=['a*', 'c*', '\gamma_y', '\gamma_z', # peak parameters
```

# Definition of mesocrystal GISAXS peak shape including instrumental resolution function and structural tilt and size distribution.

To work the data has to be defined on a regular grid, otherwise the FFT convolution algorithm won't work.

The calculations can be performed with multiprocessing, splitting each peak calculation to the different processes.

```python
from numpy import sqrt, where, arctan2, abs, exp, pi, zeros_like, unique, minimum, sin, cos
from scipy.signal import fftconvolve
from plot_script.fit_data import FitFunction3D, register_class
from multiprocessing import Pool

LAMBDA = 4.51  # Å

class PeakShapeResTilt(FitFunction3D):
    """Fit a Gaussian or Lorentzian peak function with radial tilting distribution
    and a beam shape function convoluted with fft.
    ""
    # define class variables
    name = "Mesopeak + Resolution"
    # default parameters
    parameters = [0.068, 0.021, 0.0001, 0.0001, 0.0, 0.001, 0.0, 0.0, 0.0, 0.0, 0.00531166, 0.000941805, 9233.57, 0.3, 0.1, 0.0, 0.0, 0.0]
    # names of parameters
    parameter_names=['a*', 'c*', '\gamma_y', '\gamma_z', # peak parameters
```
Appendix B Used algorithms

'σ_tilt', 'σ_r', # tilt parameter in 
'Qy_off', 'Qz_off', 'Qphi_off', # instrumental offsets 
'width', 'height', 'decay', # instrumental parameters 
'α_i', 'α_c', 
'BG', # background

fit_function_text='Meso: a**=[a*] c**=[c*] γ_y=[_y |2] γ_z=[_z |2] σ_(tilt)=[_tilt 
2]

parameter_description={'a*': 'Horizontal reciprocal lattice parameter', 
'c*': 'Vertical reciprocal lattice parameter', 
'Qy_off': 'Measurement Qy offset', 
'Qz_off': 'Measurement Qz offset', 
'Qphi_off': 'Measurement tilt offset', 
'γ_y': 'Lorenz width in Qy-direction', 
'γ_z': 'Lorenz width in Qz-direction', 
'σ_tilt': 'Width of tilting angle', 
'σ_r': 'Width of radial broughdening (distribution of 
lattice size)', 
'σ_y': 'Width of Qy broughdening (distribution of a 
parameter)', 
'σ_z': 'Width of Qz broughdening (distribution of c 
parameter)', 
'width': 'Beam width horizontal (window function)', 
'height': 'Beam width vertical (window function)', 
'decay': 'Speed of exponential intensity decay outside of 
Beam window', 
'BG': 'Background', 
}

use_rotation=True # default is an rotational average 
regions=None 
max_iter=50 # restrain the maximum number of iterations 
pool=None

def __init__(self, initial_parameters=[], use_mp=False):
    FitFunction3D.__init__(self, initial_parameters)
    self.refine_parameters=[0,1,2,3,4,5]
    self.parameter_names=list(self.parameter_names)
    self.constrains={}
    if use_mp:
        # create a pool of worker processes
        self.activate_multiprocessing()

def activate_multiprocessing(self):
    '''
    Create a worker pool.
    '''
    if self.pool is not None:
        self.deactivate_multiprocessing()
    self.pool=Pool()

def deactivate_multiprocessing(self):
    '''
    Terminate the worker pool. Must be called before exiting 
    the program, otherwise the processes stay alive and CTRL+c 
    is needed to exit the program.
    '''
    if self.pool is not None:
        self.pool.close()
        self.pool.join()
    self.pool=None

def add_region(self, xf, xt, yf, yt, Ii, Qyi, Qzi):
    '''
    Add an other peak with a defined fit region, intensity and position.
    '''
    if self.regions is None:
        self.regions=[]
    idx=len(self.regions)
    self.regions.append([xf, xt, yf, yt])
    self.parameters.append(Ii)
    self.parameters.append(Qyi)
B.4 Peak shape computation for in-situ experiments

```python
self.parameters.append(Qzi)
self.parameter_names.append("I_%i"%idx)
self.parameter_names.append("Qy_%i"%idx)
self.parameter_names.append("Qz_%i"%idx)

def fit_function(self, p, x, y):
    '''
    Combined intensity function for several peak regions including
    resolution and tilting.
    Each peak is a convolution of the resolution function a
    Gaussian/Lorentzian peak shape and a gaussian tilt and radial distribution.
    '''
    # get parameters by name
    astar=p[0]
cstar=p[1]
gamma_y=p[2]
gamma_z=p[3]
sigma_tilt=p[4]/180.*pi
sigma_r=p[5]
Qy_off=p[6]
Qz_off=p[7]
Qphi_off=p[8]/180.*pi
width=p[9]
height=p[10]
decay=p[11]
alpha_i=p[12]*pi/180.
alpha_c=p[13]*pi/180.
BG=p[14]

if self.use_rotation:
    self.parameter_names[4:6]=['σ_tilt', 'σ_r']
else:
    self.parameter_names[4:6]=['σ_y', 'σ_z']

# if no region is defined the selected fit area is taken as region
if self.regions is None:
    raise IndexError, "no peak defined"
else:
    # each region has corresponding intensity, Qy- and Qz-position parameters
    regions=[[reg[0], reg[1], reg[2], reg[3], p[15+3*i], p[16+3*i], p[17+3*i]]
             for i, reg in enumerate(self.regions)]

I=zeros_like(x)
background=zeros_like(x)
I_list=[]
param_list=[]
res_list=[]
idx_list=[]
pix_size=None

# peaks for all regions
for xf, xt, yf, yt, Ti, HK, L in regions:
    # get indices of points in the region
    idx=where((x>=xf)&(x<=xt)&(y>=yf)&(y<=yt))
    # calc position with phi offset
    Qyi=HK*astar
    Qzi=L*cstar
    Qyi=Qy_off
    Qzi=Qz_off
    # sample tilting
    Qytmp=Qy
    Qy=cos(Qphi_off)*Qytmp+sin(Qphi_off)*Qz
    Qz=-sin(Qphi_off)*Qytmp+cos(Qphi_off)*Qz

    # _ reshape x and y to two dimensional array
    ux=unique(x[idx])
    uy=unique(y[idx])
xitems=len(ux)
yitems=len(uy)
    if pix_size is None:
        pix_size=(ux[1]-ux[0])*(uy[1]-uy[0])
    # calculate pixel size for normalization
    Qy=x[idx].reshape(yitems, xitems)
    Qz=y[idx].reshape(yitems, xitems)
    # correct instrumenta>[]ll misalignment
    # 0-offset
    Qy=Qy
    Qz=Qz
    # sample tilting
    Qytmp=Qy
    Qy=cos(Qphi_off)*Qytmp+sin(Qphi_off)*Qz
    Qz=-sin(Qphi_off)*Qytmp+cos(Qphi_off)*Qz

    # initialize list
    param_list.append(p)
    I_list.append(I)
    res_list.append(res)
    idx_list.append(idx)
```

Appendix B Used algorithms

```python
in_list=[Qy, Qz, Qyi, Qzi, gamma_y, gamma_z,
sigma_tilt, sigma_r,
width, height, decay,
alpha_i, alpha_c,
l1, self.use_rotation]
idx_list.append(idx)
if self.pool is None:
    # calculate one peak
    I_list.append(calc_I(in_list))
else:
    # send calculation of one peak to the multiprocessing pool
    res_list.append(self.pool.apply_async(calc_I, args=(in_list,)))
if self.pool is not None:
    # fetch the results of the multiprocessing calculations
    I_list=map(lambda item: item.get(), res_list)
for idx, Ip in zip(idx_list, I_list):
    I[idx]+=Ip.flatten()
    background[idx]=BG
return I+background

def to_list(self):
    '''
    Get all important parameters as a list.
    '''
    return [self.parameters, self.parameter_names,
            self.regions, [self.x_from, self.x_to, self.y_from, self.y_to],
            self.refine_parameters]

def from_list(self, param_list):
    '''
    Set all important parameters from a list.
    '''
    self.parameters=list(param_list[0])
    self.parameter_names=list(param_list[1])
    self.regions=list(param_list[2])
    self.refine_parameters=list(param_list[3])

def add_mirrors(self):
    '''
    For each region add the mirror peak on the other side of the specular line.
    '''
    regions=self.regions
    regparams=[[self.parameters[15+3*i], self.parameters[16+3*i], self.parameters[17+3*i]]
               for i in range(len(regions))]
pstart=15+3*len(regions)
for i, regi, parami in zip(range(len(regions)), regions, regparams):
    self.add_region(-regi[1], -regi[0], regi[2], regi[3], parami[0], -parami[1],
                    parami[2])
    # constrain all peak parameters to the original peak
    self.constrains[pstart+3*i]=
        {'bounds': [None, None], 'tied': '[I_%i]'%i}
    self.constrains[pstart+1+3*i]=
        {'bounds': [None, None], 'tied': ['-[Qy_%i]'%i}
    self.constrains[pstart+2+3*i]=
        {'bounds': [None, None], 'tied': '[Qz_%i]'%i}
    for j in range(3):
        # fit parameter if original was selected
        if (15+j+3*i) in self.refine_parameters:
            self.refine_parameters.append(pstart+j+3*i)
    self.x_from=-self.x_to

def Qz_obs(Qz, alpha_i, alpha_c):
    k0=2.*pi/LAMBDA
    return k0*(sin(alpha_i)+
               sqrt(sin(alpha_c)**2+
               (Qz*LAMBDA/2.*pi-sqrt(sin(alpha_i)**2-sin(alpha_c)**2))**2
               ))

def gaussian_tilt(Qy, Qz, Qy0, Qz0, sigma_tilt, sigma_r):
    '''
```
B.4 Peak shape computation for in-situ experiments

Return a peak with gaussian tilt and radius components.

```python
Qr = sqrt(Qy**2 + Qz**2)
Qphi = arctan2(Qz, Qy)
Qr0 = sqrt(Qy0**2 + Qz0**2)
Qphi0 = arctan2(Qz0, Qy0)

# tilt_norm = 1/(2. * pi * sigma_r * sigma_tilt)
tilt_shape = exp(-0.5*((Qr - Qr0)/(sigma_r * Qr0))**2 +((Qphi - Qphi0)/sigma_tilt)**2)
return tilt_shape
```

```python
def beam(x, y, width, height, fall=8000., pix_size=1e-10):
    px = exp(-fall*(abs(x)-width/2.))
    py = exp(-fall*(abs(y)-height/2.))
    if height <= pix_size:
        pos = (y <= pix_size) & (y >= -pix_size)
        py[pos] = min(1. - abs(y[pos])/pix_size, 0.)
    if width <= pix_size:
        pos = (x <= pix_size) & (x >= -pix_size)
        px[pos] = min(1. - abs(x[pos])/pix_size, 0.)
    Peak = min(px, 1.) * min(py, 1.)
    return Peak
```

```python
def gaussian(x, y, sigma_x, sigma_y):
    G = exp(-0.5*((x/sigma_x)**2 + (y/sigma_y)**2))
    return G
```

```python
def lorentzian(x, y, gamma_x, gamma_y, pix_size):
    L = 1. / (1. + ((x/gamma_x)**2 + (y/gamma_y)**2))
    if gamma_x <= pix_size and gamma_y <= pix_size:
        L[pos] = 1.
    elif gamma_x <= pix_size:
        L[pos] = 1. / ((y[pos]/gamma_y)**2)
    elif gamma_y <= pix_size:
        L[pos] = 1. / ((x[pos]/gamma_x)**2)
    return L
```

```python
def calc_I(in_list):
    Qy, Qz, Qyi, Qzi = in_list[:4]
    gamma_y, gamma_z = in_list[4:6]
    sigma_tilt, sigma_r = in_list[6:8]
    width, height, decay = in_list[8:11]
    alpha_i, alpha_c = in_list[11:13]
    Ii = in_list[13]
    use_rotation = in_list[14]
    if sigma_tilt == 0:
        Ip = lorentzian(Qy-Qyi, Qz-Qzi, gamma_y, gamma_z, pix_size)
    else:
        Ip = lorentzian(Qy-Qyi, Qz-Qzi, gamma_y, gamma_z, pix_size)
```

Appendix B  Used algorithms

319  peak_shape=lorentzian(Qy-Qy.mean(), Qz-Qz.mean(), gamma_y, gamma_z, pix_size)
320  if use_rotation:
321     # calculate tilt and radial distribution function
322     gauss_shape=gaussian_tilt(Qy,Qz,Qyi,Qzi, sigma_tilt, sigma_r)
323  else:
324     # calculate gaussian distribution in Qy and Qz direction
325     gauss_shape=gaussian(Qy-Qyi,Qz-Qzi, sigma_tilt*180./pi*Qyi, sigma_r*Qzi)
326  # convolute tilt and radial distribution with peak shape
327  Ip=fftconvolve(peak_shape, gauss_shape, 'same')
328  if height!=0 and width!=0:
329     # calculate beam shape function
330     # the peak position is moved due to refraction effects
331     Qzi_obs=Qzi_obs(Qzi_obs(Qzi, alpha_i, alpha_c)
332     beam_shape=beam(Qy-Qy.mean(), Qz-Qz.mean()-Qzi_obs+Qzi, width, height, decay, pix_size)
333     # convolute peak shape with beam shape
334     Ip=fftconvolve(beam_shape, Ip, 'same')
335  return Ii*Ip/Ip.sum()  # normalize to integrated intensity
336
337  class BeamResolution(FitFunction3D):
338     '''
339     A pure resolution function to refine the peak shape with
340     e.g. silicon total reflection measurement.
341     '''
342     name="Resolution"
343     parameters=[10000. , 0. , 0.177 , 0.009318059 , 9233.57]
344     parameter_names=['I0 ', 'x0 ','y0 ','width ' ,' height ','decay ']
345     fit_function_text='Resolution'
346     def fit_function(self, p, x, y):
347         I0,x0,y0,w,h,d=p
348         return I0*beam(x-x0,y-y0,w,h,d)
349     # Add class to the available fit functions in Plot.py
350     register_class(PeakShapeResTilt)
351     register_class(BeamResolution)
352     #
356     #
357 # B.5 GeniX plugin for a reflectivity simulation of an
358 # ensemble of mesocrystals

B.5 GeniX plugin for a reflectivity simulation of an
ensemble of mesocrystals

1  '''
2  # Simulating nanoparticle assemblies.
3  '''
4  from numpy import *
5  from lib.paratt as Paratt
6  from lib.neutron_refl as MatrixNeutron
7  from lib.instrument import *
8  # Preamble to define the parameters needed for the models outlined below:
9  ModelID='SpecNX'
10  __pars__=['Layer', 'Stack', 'Sample', 'Instrument']
11  instrument_string_choices={
12   'probe': ['x-ray', 'neutron', 'neutron pol', 
13     'neutron pol spin flip', 'neutron tof', 'neutron pol tof'],
14   ' coords': ['q', 'tth'],
15   'restype': ['no conv', 'fast conv',
16     'full conv and varying res.', 'fast conv + varying res.'],
17   'footype': ['no corr', 'gauss beam', 'square beam'],
18   'pol': ['uu', 'dd', 'ud']}
19  InstrumentParameters={
20     'probe': 'x-ray', ' wavelength':1.54, ' coords': 'q',
21     'instrument': 'SpecNX',
22     'stack': 1, 'sample': 1, 'instrument': 'SpecNX',}
B.5 GeniX plugin for a reflectivity simulation of an ensemble of mesocrystals

```python
InstrumentGroups=[(['General', ['wavelength', 'coords', 'I0', 'Ibg', 'coherence_length']],)
    ('Resolution', ['restype', 'res', 'respoints', 'resinrange']),
    ('Neutron', ['probe', 'pol', 'incangle']),
    ('Footprint', ['footype', 'beamw', 'samplelen']),)

InstrumentUnits={'probe': '', 'wavelength': 'AA', 'coords': '', 'I0': 'arb.', 'res': '[coord]', 'coherence_length': 'AA',
    'restype': '', 'respoints': 'pts.', 'resinrange': '[coord]', 'beamw': 'mm',
    'footype': '', 'samplelen': 'mm', 'incangle': 'deg.', 'pol': '',
    'Ibg': 'arb.'}

LayerParameters={'sigma': 0.0, 'dens': 1.0, 'd': 0.0, 'f': (1.0 + 1.0j) * 1e-20,
    'b': 0.0 + 1.0j, 'xs_ai': 0.0, 'magn': 0.0, 'magn_ang': 0.0,
    'np_z_position': 0.5, 'np_type': 0}

LayerUnits={'sigma': 'AA', 'dens': 'at./AA', 'd': 'AA', 'f': 'el./at.,
    'b': 'fm/atom', 'xs_ai': 'barn/atom', 'magn': 'mu_B/atom', 'magn_ang': 'deg.,
    'np_z_position': '', 'np_type': '0/1'}

LayerGroups=[('Standard', ['f', 'dens', 'd', 'sigma']),
    ('Neutron', ['b', 'xs_ai', 'magn', 'magn_ang']),
    ('Particles', ['np_z_position', 'np_type'])]

StackParameters={'Layers': [], 'Repetitions': 1, 'slices': 10, 'is_meso': 0,
    'r_bottom': 1500., 'r_top': 1000., 'surface_density': 25.,
    'c_bottom': 100., 'c_top': 100., 'c_var_layers': 5, 'aspect_ratio': 1.,
    'f_matrix': 0.0j, 'dens_matrix': 1., 'b_matrix': 0.0j, 'magn_matrix': 0.,
    'magn_ang_matrix': 0.)

StackUnits={'Repetitions': '', 'slices': '', 'is_meso': '0/1',
    'r_bottom': 'AA', 'r_top': 'AA', 'surface_density': '%',
    'c_bottom': 'AA', 'c_top': 'AA', 'c_var_layers': '', 'aspect_ratio': 'c/a',
    'f_matrix': 'et./at.', 'dens_matrix': 'at./AA',
    'b_matrix': 'fm/atom', 'magn_matrix': 'mu_B/atom', 'magn_ang_matrix': 'deg.,
    '}

SampleParameters={'Stacks': [], 'Ambient': None, 'Substrate': None}
```

# define the density profiles for the different types of particles
# density is defined as particle surface in a layer

def profile_sphere(idp, d):
    r = d/2.
    return where(abs(idp) < r, (pi*(r**2 - idp**2)), 0.)

def profile_cube(idp, a):
    return abs(idp) <= a)*a**2

DENSITY_PROFILES=[profile_sphere, profile_cube]

SINGLE_PART=1

# A buffer to save previous calculations for spin-flip calculations

class Buffer:
    Ruu=0
    Rdd=0
    Rdu=0
    Rud=0
    parameters=None

def Specular(TwoThetaQz, sample, instrument):
    # calculate the reflectivity for the different parts of the sample
```
Appendix B  Used algorithms

```python
# which lie in one correlation area (top of meso, edges of mesos, bottom)
meso=None
for stack in reversed(sample.Stacks):
    if stack.is_meso:
        meso=stack
        break
if meso is None:
    # simulation without mesos
    R=SpecRaw(TwoThetaQz, sample, instrument)
    return SpecRes(TwoThetaQz, sample, instrument, R)

    # calculate intensity for space between mesos
    meso.dens_bottom=0.0
    meso.dens_top=0.0
    Rfree=SpecRaw(TwoThetaQz, sample, instrument)

    # calculate intensity for meso edges
    # if the slope is lower than the coherence length/2
    # it gets calculated in several steps
    if (meso.r_bottom - meso.r_top) >=(instrument.coherence_length /2.) :
        r_steps=arange (meso.r_top ,
                        meso.r_bottom + instrument.coherence_length/2.,
                        instrument.coherence_length/2.)
        F1=(meso.r_top - instrument.coherence_length/2.)*2/
            (meso.r_bottom + instrument.coherence_length/2.)*2
        Psteps=r_steps[1:]-r_steps[: -1]) * 2/F1
        Psteps/=Psteps[: -1].sum()
        Redge=zeros_like ( Rfree )
        for i, ri in enumerate ( r_steps[: -1]) :
            meso.dens_top =( meso.r_bottom **2 -(ri + instrument.coherence_length/2.) **2) /(
                           meso.r_bottom **2 -meso.r_top **2)
            meso.dens_bottom =( meso.r_bottom **2 -(ri - instrument.coherence_length/2.) **2) /(
                           meso.r_bottom **2 -meso.r_top **2)
            Redge += Psteps[i]* SpecRaw ( TwoThetaQz , sample , instrument )
        else :
            meso.dens_top =0.5*(1. -( meso.r_top / meso.r_bottom ))
            meso.dens_bottom =0.5*(1+( meso.r_top / meso.r_bottom ))
            Redge = SpecRaw ( TwoThetaQz , sample , instrument )

    # calculate intensity for meso center
    meso.dens_bottom=1.0
    meso.dens_top=1.0
    Rtop=SpecRaw(TwoThetaQz, sample, instrument)

    # combine intensities
    meso_outer_area=(meso.r_bottom + instrument.coherence_length/2.)*2
    meso_inner_area=min ((meso.r_top - instrument.coherence_length/2. , 0.))*2
    full_area=meso_outer_area/meso.surface_density*100.  # full area is mesocrystal/ 
                                                          # mc-density
    free_area=full_area-meso_outer_area
    edge_area=meso_outer_area-meso_inner_area
    if SINGLE_PART<0:
        # combined reflectivity
        R=free_area/full_area*Rfree+meso_inner_area/full_area*Rtop+edge_area/full_area
        *Redge
    elif SINGLE_PART==1:
        R=Rfree
    elif SINGLE_PART==2:
        R=Redge
    else:
        R=Rtop
    # for SLD use some kind of approximation
    meso.dens_bottom=1.-free_area/full_area
    meso.dens_top=(1.-full_area/full_area)* (meso.r_top **2/meso.r_bottom **2)
# Resolution corrections and return
return SpecRes(TwoThetaQz, sample, instrument, R)

def SpecRaw(TwoThetaQz, sample, instrument):
    # preamble to get it working with my class interface
    restype=instrument.getRestype()
    if restype==2 or restype==instrument_string_choices[retype][2]:
        (TwoThetaQz, ignore)=ResolutionVector(TwoThetaQz[:], \
                                                instrument.getRes(), instrument.getRespoints(), \
```
```
B.5 GeniX plugin for a reflectivity simulation of an ensemble of mesocrystals

```python
# TTH values given as x
if instrument.getCoords() == instrument_string_choices['coords'][1]
    or instrument.getCoords() == 1:
    Q = 4*pi/instrument.getWavelength()*sin(TwoThetaQz*pi/360.0)
# Q vector given....
e elif instrument.getCoords() == instrument_string_choices['coords'][0]
    or instrument.getCoords() == 0:
    Q = TwoThetaQz
else:
    raise ValueError('The value for coordinates, coords, is WRONG!
    ' should be q(0) or tth(1).')

type_ = instrument.getProbe()
pol = instrument.getPol()

# lambda = instrument.getWavelength()
parameters = sample.resolveLayerParameters()
if type_ == instrument_string_choices['probe'][0] or type_ == 0:
    fb = array(parameters['f'], dtype=complex64)
else:
    fb = array(parameters['b'], dtype=complex64).real*1e-5
    abs_xs = array(parameters['xs_ai'], dtype=complex64)*1e-4**2
    d = array(parameters['d'], dtype=float64)
    magn = array(parameters['magn'], dtype=float64)
# Transform to radians
magn_ang = array(parameters['magn_ang'], dtype=float64)*pi/180.0
sigma = array(parameters['sigma'], dtype=float64)

if type_ == instrument_string_choices['probe'][0] or type_ == 0:
    sld = dens*fb*instrument.getWavelength()**2/2/pi
else:
    wl = instrument.getWavelength()
    sld = dens*(wl**2/2/pi*sqrt(fb**2-(abs_xs/2.0/wl)**2)-
        1.0*abs_xs*wl/4/pi)
# Ordinary Paratt X-rays
elif type_ == instrument_string_choices['probe'][0] or type_ == 0:
    R = Paratt.ReflQ(Q, instrument.getWavelength(), 1.0-2.82e-5*sld, d, sigma)
# Ordinary Paratt Neutrons
elif type_ == instrument_string_choices['probe'][1] or type_ == 1:
    R = Paratt.ReflQ(Q, instrument.getWavelength(), 1.0-sld, d, sigma)
# Ordinary Paratt but with magnetization
elif type_ == instrument_string_choices['probe'][2] or type_ == 2:
    msld = 2.645e-5*magn* dens*instrument.getWavelength()**2/2/pi
    if pol == instrument_string_choices['pol'][0] or pol == 0:
        R = Paratt.ReflQ(Q, instrument.getWavelength(), 
            1.0-sld-msld, d, sigma)
    else:
        raise ValueError('The value of the polarization is WRONG.
        ' It should be uu(0) or dd(1).')
# Spin flip
elif type_ == instrument_string_choices['probe'][3] or type_ == 3:
    # Check if we have calculated the same sample previous:
    if Buffer.parameters != parameters:
        msld = 2.645e-5*magn* dens*instrument.getWavelength()**2/2/pi
        np = 1.0-sld-msld
        nm = 1.0-sld+msld
        wl = instrument.getWavelength()
        (Ruu, Rdd, Rud, ignore) = MatrixNeutron.Refl(Q, wl, np, nm, d, magn_ang)
        Buffer.Ruu = Ruu; Buffer.Rdd = Rdd; Buffer.Rud = Rud
        Buffer.parameters = parameters.copy()
    else:
        pass
```
Appendix B Used algorithms

```python
# Polarization uu or ++
if pol == instrument_string_choices['pol'][0] or pol == 0:
    R = Buffer.Ruu
elif pol == instrument_string_choices['pol'][1] or pol == 1:
    R = Buffer.Rdd
elif pol == instrument_string_choices['pol'][2] or pol == 2:
    R = Buffer.Rud
else:
    raise ValueError('The value of the polarization is WRONG.
    It should be uu (0), dd (1) or ud (2)')

# tof
elif type_ == instrument_string_choices['probe'][4] or type_ == 4:
    wl = 4*pi*instrument.getIncangle()*pi/180/Q
    sld = dens[:, newaxis]*(wl**2/2/pi*sqrt(fb[:, newaxis]**2-
                            (abs_xs[:, newaxis]*2.0/wl)**2) -
                            1.0*abs_xs[:, newaxis]*wl/4/pi)
    R = Paratt.Refl_nvary2(instrument.getIncangle()*ones(Q.shape),
                            (4*pi*instrument.getIncangle()*pi/180/Q),
                            1.0-sld, d, sigma)

# tof spin polarized
elif type_ == instrument_string_choices['probe'][5] or type_ == 5:
    wl = 4*pi*instrument.getIncangle()*pi/180/Q
    sld = dens[:, newaxis]*(wl**2/2/pi*sqrt(fb[:, newaxis]**2-
                            (abs_xs[:, newaxis]*2.0/wl)**2) -
                            1.0*abs_xs[:, newaxis]*wl/4/pi)
    msld = 2.645e-5*magn[:, newaxis]*dens[:, newaxis]*
                            (4*pi*instrument.getIncangle()*pi/180/Q)**2/2/pi
    sld = sld - msld
if pol == instrument_string_choices['pol'][0] or pol == 0:
    R = Paratt.Refl_nvary2(instrument.getIncangle()*ones(Q.shape),
                            (4*pi*instrument.getIncangle()*pi/180/Q),
                            1.0-sld, d, sigma)
elif pol == instrument_string_choices['pol'][1] or pol == 1:
    R = Paratt.Refl_nvary2(instrument.getIncangle()*ones(Q.shape),
                            (4*pi*instrument.getIncangle()*pi/180/Q),
                            1.0-sld, d, sigma)
else:
    raise ValueError('The value of the polarization is WRONG.
    It should be uu(0) or dd(1)')

else:
    print type_
    raise ValueError('The choice of probe is WRONG')

return R

def SpecRes(TwoThetaQz, sample, instrument, R):
    # preamble to get it working with my class interface
    restype = instrument.getRestype()
    if restype == 2 or restype == instrument_string_choices['restype'][2]:
        (TwoThetaQz, weight) = ResolutionVector(TwoThetaQz[:],
                                                instrument.getRes(),
                                                instrument.getRespoints(),
                                                range_=instrument.getResinrange())
    # TTH values given as x
    if instrument.getCoords() == instrument_string_choices['coords'][1]:
        Q = 4*pi/instrument.getWavelength()*sin(TwoThetaQz*pi/360.0)
    # Q vector given
    else:
        raise ValueError('The value for coordinates, coords, is WRONG!
        It should be q(0) or tth(1).')

    type_ = instrument.getProbe()
    pol = instrument.getPol()
    # lambd = instrument.getWavelength()
```
B.5 GeniX plugin for a reflectivity simulation of an ensemble of mesocrystals

```python
# parameters = sample_resolveLayerParameters()
# if type_ == instrument_string_choices['probe'][0] or type_ == 0:
#    fb = array(parameters['f'], dtype = complex64)
# else:
#    fb = array(parameters['b'], dtype = complex64).real*1e-5
# abs_xs = array(parameters['xs_ai'], dtype = complex64)*(1e-4)**2

# Footprint Corrections
foocor=1.0
footype=instrument.getFootype()
beamw=instrument.getBeamw()
samlen=instrument.getSamplelen()
theta=arcsin(Q*instrument.getWavelength()/4.0/pi)*180/pi
if footype == 1 or footype == instrument_string_choices['footype'][1]:
    foocor=GaussIntensity(theta, samlen/2.0, samlen/2.0, beamw)
elif footype == 2 or footype == instrument_string_choices['footype'][2]:
    foocor=SquareIntensity(theta, samlen, beamw)
elif footype == 0 or footype == instrument_string_choices['footype'][0]:
    pass
else:
    raise ValueError('The choice of footprint correction, footype, is WRONG')

# Resolution corrections
if restype == instrument_string_choices['restype'][1] or restype == 1:
    R=ConvoluteFast(TwoThetaQz, R[:,]*foocor, instrument.getRes(),
    range_=instrument.getResintrange())
elif restype == instrument_string_choices['restype'][2] or restype == 2:
    R=ConvoluteResolutionVector(TwoThetaQz, R[:,]*foocor, weight)
elif restype == instrument_string_choices['restype'][3] or restype == 3:
    R=ConvoluteFastVar(TwoThetaQz, R[:,]*foocor, instrument.getRes(),
    range_=instrument.getResintrange())
elif restype == instrument_string_choices['restype'][0] or restype == 0:
    R=R[:,]*foocor
else:
    raise ValueError('The choice of resolution type, restype, is WRONG')

return R*instrument.getI0()+instrument.getIbkg()

def OffSpecularMingInterdiff(TwoThetaQz, ThetaQx, sample, instrument):
    raise NotImplementedError('Not implemented use model interdiff insteads')
    return TwoThetaQz, ThetaQx

def SLD_calculations(z, sample, inst):
    ''' Calculates the scatteringlength density as at the positions z
    ...'
    parameters = sample_resolveLayerParameters()
    dens = array(parameters['dens'], dtype = complex64)
    f = array(parameters['f'], dtype = complex64)
    b = array(parameters['b'], dtype = complex64)
    type_ = inst.getProbe()
    magnetic = False
def_sld=0
    if type_ == instrument_string_choices['probe'][0] or type_ == 0:
        sld = dens*f
def_sld=0
    elif type_ == instrument_string_choices['probe'][1] or type_ == 1 or
    type_ == instrument_string_choices['probe'][4] or type_ == 4:
        sld = dens*b
def_sld=0
    else:
        magnetic = True
def_sld=0
        sld = dens*b
    magn = array(parameters['magn'], dtype = float64)
    # Transform to radians

    def_sld=0
    #include one extra element — the zero pos (substrate/film interface)
    int_pos = cumsum(r_[0, d])
```

207
Appendix B Used algorithms

372 sigma = array (parameters['sigma'], dtype=float64)[:-1]+1e-7
373 if z is None:
374 z = arange (-sigma[0]*5, int_pos.max()+sigma[-1]*5, 0.5)
375 if not magnetic:
376 rho = sum ((sld[:-1]-sld[1:])*0.5-0.5*erf((z[:, newaxis]-int_pos)/sqrt(2.)/sigma)), 1)+sld[-1]
377 else:
378 sld_p = sld+mag_sld
379 sld_m = sld-mag_sld
380 rho_p = sum ((sld_p[:-1]-sld_p[1:])*0.5-0.5*erf((z[:, newaxis]-int_pos)/sqrt(2.)/sigma)), 1)+sld_p[-1]
381 rho_m = sum ((sld_m[:-1]-sld_m[1:])*0.5-0.5*erf((z[:, newaxis]-int_pos)/sqrt(2.)/sigma)), 1)+sld_m[-1]
382 dicit = ('real sld': real(rho), 'imag sld': imag(rho), 'z': z)
383 return dicit

SimulationFunctions = {'Specular': Specular, 'OffSpecular': OffSpecularMingInterdiff, 'SLD': SLD_calculations}

import lib.refl as Refl

(Instrument, Layer, Stack, Sample) = Refl.MakeClasses(InstrumentParameters, LayerParameters, StackParameters, SampleParameters, SimulationFunctions, ModelID)

def resolveLayerParameter(self, parameter):
    # if stack type includes nanoparticles, the parameters consist of slices
    if self.is_meso:
        # c-parameter variation from bottom to top. lower layers stay constant
        c_all = [self.c_bottom]*int(max([(self.Repetitions-self.c_var_layers), 0]))+
                linspace(self.c_bottom, self.c_top, min([self.c_var_layers, self.Repetitions])).tolist()
        if parameter == 'd':
            par = []
            for ci in c_all:
                par += [ci/self.slices]*int(self.slices)
        elif parameter == 'dens':
            par = [1.0]*int(self.Repetitions*self.slices)
        elif parameter == 'sigma':
            par = []
            for ci in c_all:
                par += [ci/self.slices/2.]*int(self.slices)
        else:
            SLD_matrix = getattr(self, parameter+'_matrix')*self.dens_matrix
            # The mesos can be more dense at bottom than at top
            # The dens_bottom and dens_top parameters are set during the intensity calculations.
            # The density of the lowest layer is always 1.
            dens_all = [1./(self.c_bottom/self.aspect_ratio)**2]*
                        linspace(getattr(self, 'dens_bottom', 1.)/(self.c_bottom/
                        self.aspect_ratio)**2, self.aspect_ratio)**2,
                        getattribute(self, 'dens_top', 1.)/(self.c_top/self.
                        aspect_ratio)**2, self.Repetitions).tolist()
            for i, dens_from_to in enumerate(zip(dens_all[:-1], dens_all[1:])):
                dens = linspace(dens_from_to[0], dens_from_to[1], self.slices)
                pari = (SLD_matrix*dens)
                self.layers[i].calculate_slices(parameter, c_all[i], pari, SLD_matrix*dens[0], dens,
                bottom=(i==0), top=(i==self.Repetitions-1))
                par += pari.tolist()
    else:
        par = [0.0]*int(self.Repetitions*self.slices)
    else:
        par = [lay.__getattribute__('_')(parameter)+0.0 for lay in self.layers]*self.Repetitions
    return par

208
## B.5 GeniX plugin for a reflectivity simulation of an ensemble of mesocrystals

```python
def calculate_slices(self, parameter, c, slices, matrix, dens, bottom=True, top=False):
    ''' Calculate the SLD profile for one nanoparticle layer as a
    sum of all profiles from the particles inside.
    '''
    SLD = getattr(self, parameter) * self.dens
    d = c / len(slices)
    sigma = self.sigma
    # smear out the position of the particles
    if sigma == 0:
        d_pos = [0.]
        P_pos = [1.]
    else:
        d_pos = arange(-2 * sigma, 2 * sigma + d / 2., d / 2.)
        P_pos = exp(-0.5 * d_pos ** 2 / sigma ** 2)
        P_pos /= P_pos.sum()
    # structure types
    profile = DENSITY_PROFILES[int(self.np_type)]
    # calculate SLDs
    if bottom:
        dens = [dens[0]] * len(dens)
        tmp_slice = zeros_like(slices)
        pos = arange(len(slices)) * d
        for deli, Pi in zip(d_pos, P_pos):
            # position of the slice
            # center position of the nanoparticle
            np_pos = self.np_z_position * c + deli
            idp = pos - np_pos
            tmp_slice += Pi * (SLD - matrix) * profile(idp, self.d) * dens
    if not bottom:
        # particle parts sticking out from the lower lying UC
        tmp_slice += Pi * (SLD - matrix) * profile(idp + c, self.d) * dens
    if not top:
        # particle parts sticking out from the higher lying UC
        tmp_slice += Pi * (SLD - matrix) * profile(idp - c, self.d) * dens
    slices += tmp_slice
    # for i in range(len(slices)):
    #    tmp_slice = 0.
    #    for deli, Pi in zip(d_pos, P_pos):
    #        # position of the slice
    #        # center position of the nanoparticle
    #        np_pos = self.np_z_position * c + deli
    #        idp = pos - np_pos
    #        tmp_slice += Pi * (SLD - matrix) * profile(idp, self.d) * dens[i]
    #    if not bottom:
    #        # particle parts sticking out from the lower lying UC
    #        tmp_slice += Pi * (SLD - matrix) * profile(idp + c, self.d) * dens[i]
    #    if not top:
    #        # particle parts sticking out from the higher lying UC
    #        tmp_slice += Pi * (SLD - matrix) * profile(idp - c, self.d) * dens[i]
    #    slices[i] += tmp_slice

Layer.calculate_slices = calculate_slices
Stack.resolveLayerParameter = resolveLayerParameter

if __name__ == '__main__':
    pass
```
Appendix C

Bibliography

Books


Appendix C Bibliography

**Articles**


213


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Appendix C Bibliography


**Other Publications**


## Appendix D

### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>General scattering geometry for a scattering event of a particle with incoming wavevector $k_i$, outgoing wavevector $k_f$ and with an outgoing angle $2\theta$. The angles $\phi$, $\omega$ define the angle of the sample (see figure 2.4).</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>Application of the convolution theorem to simplify the modeling and allow a model independent understanding of a scattering experiment.</td>
<td>20</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic view of an Ewald sphere.</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Geometry of a scattering experiment with different rotation axis (blue arrows) and their corresponding angles.</td>
<td>22</td>
</tr>
<tr>
<td>2.5</td>
<td>Geometry of a specular and off-specular scattering experiment.</td>
<td>24</td>
</tr>
<tr>
<td>2.6</td>
<td>Geometry of a grazing incidence small angle scattering experiment (GISAS).</td>
<td>24</td>
</tr>
<tr>
<td>3.1</td>
<td>Example picture of a light microscope image with 50x magnification and a resolution of 1.8 $\mu$m (inset: 1000x, 0.3 $\mu$m).</td>
<td>28</td>
</tr>
<tr>
<td>3.2</td>
<td>Comparison between SEM pictures using the TLD and the vCD detector. The pictures have been recorded simultaneously.</td>
<td>29</td>
</tr>
<tr>
<td>3.3</td>
<td>The sample structure before the plasma treatment, where the structure can only be estimated. The picture inset shows an equivalent position of the same sample after applying the plasma. A good contrast between the nanoparticles is visible.</td>
<td>29</td>
</tr>
<tr>
<td>3.4</td>
<td>Example pictures for every operating mode: The HRTEM (a) picture shows a high resolution image of spherical particles, where the lattice planes are visible. The TEM picture yields information about the stacking of the nanoparticle layer perpendicular to the substrate. (b) shows an imperfectly aligned specimen, where the nanoparticles are aligned off-zone and the silica in-zone. (c) shows a TEM picture where the nanoparticles are aligned in-zone. The inset shows a SEAD pattern containing information about the nanoparticle orientation inside the mesocrystal.</td>
<td>31</td>
</tr>
<tr>
<td>3.5</td>
<td>Example pictures for a height profile in different magnifications measured with an AFM in non contact mode.</td>
<td>32</td>
</tr>
<tr>
<td>3.6</td>
<td>Setup of the Bruker D8 reflectometer</td>
<td>33</td>
</tr>
<tr>
<td>3.7</td>
<td>Setup of the SAXS instrument</td>
<td>34</td>
</tr>
<tr>
<td>3.8</td>
<td>General setup of an GISAXS instrument</td>
<td>35</td>
</tr>
<tr>
<td>3.9</td>
<td>Setup for a diffraction experiment- here the inhouse 4circle diffractometer.</td>
<td>37</td>
</tr>
<tr>
<td>4.1</td>
<td>SAXS from spherical particles $S_{0.1}^{0.1}$ fitted with a spherical FF. The fit parameters are shown in table 4.2.</td>
<td>45</td>
</tr>
</tbody>
</table>
Appendix D  List of Figures

4.2  SAXS from cubic nanoparticles \( S_0^{0.1} \) fitted with a spherical, truncated cubes and rounded cubes form factor. The fit parameters are shown in table 4.2. ................................. 45
4.3  TEM pictures of the used particles, deposited on a TEM grid. ................................. 46
4.4  Schematics of the various applied magnetic fields. .................................................. 47
4.5  Samples produced under the same conditions. ....................................................... 48
4.6  Schematic illustration of the model of the self-assembly of an ensemble of mesocrystals. The red box illustrates one nucleation area, which is magnified in the last two pictures. .................................................. 50
4.7  Schematics of the size dependent bonding formation in a vacancy of a regular nanoparticle superlattice. .................................................. 51
4.8  Illustration of characteristics of the mesocrystal self-assembly: Layer-by-layer growth can be assumed in these SEM pictures, where the layers are not closed because of an interrupted mesocrystal growth after drying due to low solution concentration. .................................................. 52
4.9  Illustration of characteristics of the mesocrystal self-assembly measured by SEM: The residual particles are shown on the base layer (figure 4.9a). The size dependent self-assembling is also observed in figure 4.9a, despite the small number of particles. Gaps in the base layer can be seen in figure 4.9b. Figure 4.9c, figure 4.9d illustrate the dependence of the shape of the mesocrystal on the geometry of the unit cell from the nanoparticle superstructure. A more cylindrical/hexagonal shape is grown for spheres and quadratic shape for cubes with small degree of truncation. Figure 4.9d shows also cracks inside the mesocrystal by higher magnification like the crystal consisting of spheres. .................................................. 53
4.10 Illustration of characteristics of the mesocrystal self-assembly: A mesocrystal growth with and without inclined edges can be observed by AFM. The insets in the AFM pictures show a cross section for better illustration. .................................................. 54
4.11 Ensemble of mesocrystals measured with AFM for its topography (bottom). The right SEM image shows a view from the top and the left picture shows the nanoparticle order on top of one mesocrystal with higher magnification. .................................................. 55
4.12 Structural analysis of an ensemble of mesocrystals formed with long waiting time from spherical building blocks of radius 5.01 nm self-assembled under a magnetic field of 80 mT and gradient up. The measurement was done under an angle of 0.4° and with a wavelength of 1.77 Å. Reflections of the GISAXS pattern are indexed according to the rhombohedral structure discussed in the text. The Bragg peaks resulting from scattering of the reflected beam are weak under this angle and not indexed. The SEM picture is made from the top of a mesocrystal, the TEM picture shows a vertical cut through a mesocrystal and therefore a plane perpendicular to the substrate. .................................................. 57
4.13 Structural analysis of an ensemble of mesocrystals formed with extra long waiting time from cubic building blocks of edge length 10.9 nm and degree of truncation of 0.8 self-assembled without a magnetic field. The measurement was done under an angle of 0.4° and with a wavelength of 1.54 Å. Reflections of the GISAXS pattern are indexed according to the tetragonal structure discussed in the text. The Bragg peaks resulting from scattering of the reflected beam are weak at this angle and not indexed. The SEM picture is made from the top of a mesocrystal, the TEM picture shows a vertical cut through a mesocrystal and therefore a plane perpendicular to the substrate. .................................................. 58
4.14 Schematic unit cell of the rhombohedral structure of the nanospheres (left) and the body centered tetragonal (right) structure of nanocubes mesocrystal. 

4.15 Ensembles of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml at different field conditions (low field: gray; strong field: black, gradient up, gradient in-plane, gradient down, without field, homogenous field perpendicular to the sample surface). The measurements were performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.16 Ensembles of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $4.7 \times 10^{14}$ NP/ml at different field conditions (low field: gray; strong field: black, gradient up, gradient in-plane, gradient down, without field, homogenous field perpendicular to the sample surface). The measurements were performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.17 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 80 mT and gradient up. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.18 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 80 mT and gradient down. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil. Peaks originating from a rotation of the main structure and their original positions are marked.

4.19 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 2 mT and gradient up. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.20 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a magnetic field of 2 mT and gradient down. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.21 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml in a homogeneous magnetic field of 4 mT perpendicular to the sample surface. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.

4.22 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration $8.4 \times 10^{14}$ NP/ml without applied magnetic field. The GISAXS measurement was performed at an angle of incidence of 0.4° and with a wavelength of 1.77 Å at SWING, Soleil.
4.23 Ensemble of mesocrystals self-assembled with long waiting time from spherical building blocks of radius 5.01 nm and concentration 8.4·10^{14} NP/ml in a magnetic field of 2 mT and gradient in-plane. The GISAXS measurement was performed at an angle of incidence of 0.4 ° and with a wavelength of 1.77 Å at SWING, Soleil.

4.24 Ensemble of mesocrystals built up by cubic building blocks of edge length 10.9 nm and degree of truncation of 0.8 self-assembled within 12 min. The measurement was performed at an angle of 0.3 ° and with a wavelength of 1.27 Å.

4.25 Ensemble of mesocrystals built up by cubic building blocks of edge length 10.9 nm and degree of truncation of 0.8 self-assembled within 250 min. The measurement was performed at an angle of 0.3 ° and with a wavelength of 1.27 Å. Some reflexes of the second structure are marked with black points.

4.26 Ensemble of mesocrystals built up by spherical building blocks self-assembled with shorter and longer evaporation time for a gradient down configuration. The measurement was performed at an angle of 0.4 ° and with a wavelength of 1.54 Å.

4.27 Ensemble of mesocrystals self-assembled from spherical and cubic building blocks at once self-separated into mesocrystals. The result of the shape induced self-segregation is shown in the SEM pictures with obvious structural diversity on top of different mesocrystals (the overview at lower magnification is shown here), as well as in the existence of sharp mesocrystals GISAXS peaks of two different space groups.

4.28 Ensemble of mesocrystals self-assembled from spherical and cubic building blocks at once self-separated into mesocrystals. The result of the shape induced self-segregation is shown in the SEM pictures with obvious structural diversity on top of different mesocrystals. The darker areas are the results of a charging effect from previous higher resolutions scans.

4.29 Light microscopy images of an ensemble of mesocrystals self-assembled under an in-plane magnetic field of 30 mT and gradient of 70 mT/cm. The arrow shows the direction of the field lines.

4.30 Images of a macroscopic poly-mesocrystal self-assembled from γ-Fe₂O₃ nanoparticles.

4.31 SEM images of a macro-polycrystal self-assembled with γ-Fe₂O₃ nanoparticles with different magnifications.

4.32 GISAXS/SAXS measurements of a macro-polycrystal self-assembled with γ-Fe₂O₃ nanoparticles at the lab source in Risø. The measurement was done in transmission geometry (a) and under an angle of 0.4 ° (b) with a wavelength of 1.54 Å.

4.33 SEAD pattern of one mesocrystal with its corresponding real space TEM image for spherical and for cubic building blocks. The SEAD images are taken from around a 10x10 nanoparticle cluster from the mesocrystal mapped. The white arrow with the letter n defines the growth direction of the mesocrystal.
4.34 X-ray diffraction measurements of an ensemble of mesocrystals with different building blocks. The $\omega - 2\theta$ scans run from $0^\circ$ to $100^\circ$ scattering angle and are shown in the overview plot. The small angle part (inset on the left side) shows the good structure of the nanoparticle superstructure, while the wide angle part (inset on the right side) is sensitive to the atomic structure of the particles inside the mesocrystals and illustrates the alignment of the crystalline orientation inside the mesocrystals averaged over the ensemble. The black indices correspond to the $\gamma$-$\text{Fe}_2\text{O}_3$ crystal lattice, the gray one for silicon reflexes from the substrate (spheres: (400) Si reflex; cubes: (111), (222) and (333) Si reflexes; all reflexes produce multiple peaks due to other wavelength contamination in the X-ray beam).

4.35 $\chi$-scan on the (004) peak found in the $\omega - 2\theta$ scan (blue) and symmetric positions around the peak (red and green) are shown. In this configuration the scan is done in tangential direction, which is lying parallel to $Q_y$ without changing of $|\vec{Q}|$. The Gauß-fit (pink) results in a peak width $\sigma$ of $5.5^\circ$.

5.1 The geometric representation of the two different kinds of cubic form factors in real space. The definition and some example values for the degree of truncation $\tau$ is shown.

5.2 Cubic particles ordered in on a mesocrystal with deviation of the particle position (SEM picture on top of a mesocrystal).

5.3 Influence of size distributed ensemble of mesocrystals on the peak shape.

5.4 The complexity of the mesocrystal ensemble is shown as examples in these SEM and LM pictures. The shape deviation is illustrated in figure 5.4a, 5.4b and 5.4c, in which figure 5.4a and 5.4b exist in one sample. Figure 5.4d is an example for the out-of-plane rotation which is observed. The variation of the mesocrystal distances is shown in figure 5.4e and 5.4f.

5.5 The three components used to compute the peak shape with FFT.

5.6 Sketch of the model for the particle density at a given position and the different parameters used in eqn. 5.12-5.14. For the case of closed packed spheres and body centered tetragonal cubes the model parameters indicated are: Position of the model slice $z$, individual particles $z_i$, spheres radius $r$, cubes edge length $a$ and unit cell cross section $S_{UC}$.

5.7 Sketch of the surfaces simulated in the reflectivity model.

5.8 Example of simulated reflectivity with each sub-model. The red labels describes the X-ray data and the blue one correspond to the neutron data. The black points are the measured data. Edge, free and center correspond to the parts referred to as $S_{edge}$, $S_{free}$, $S_{center}$ in eqn. 5.15-5.17, the contribution of the different regions of the mesocrystal. Full is the weighted sum of all components $I_R$ from eqn. 5.15. The sample is an ensemble of mesocrystals formed with extra long waiting time from spherical building blocks of radius $5.01 \text{ nm}$ self-assembled under an magnetic field of $2 \text{ mT}$ and gradient up. The measurement was done with a wavelength of $4.73 \AA$ for neutrons and $1.54 \AA$ for X-rays.
5.9 BornAgain simulation of the GISAXS scattering intensity of an ensemble of mesocrystals formed with long waiting time from spherical building blocks of radius 5.01 nm self-assembled under a magnetic field of 80 mT and gradient up. The measurement was done under an angle of 0.4° and with a wavelength of 1.77 Å at SWING/Soleil. 98

6.1 In situ cell used in the experiment. Different components are marked with letters, which are explained in the text. The inset shows the view from the microscope camera (f) on the substrate. 102

6.2 Experimental setup at the ID01 beamline (see section 3.7) including the new developed in-situ cell. The features of the cell are described in section 6.1. 103

6.3 Different geometries used at ID01 beamline. 104

6.4 Results from SAXS measurements. 105

6.5 Time evolution of the GISAXS pattern during a middle evaporation time for spherical particles. The insets show the (015) reflex enlarged in a linear scale. The text insets on the right side indicates the time. 106

6.6 Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same $\sigma_r$, $\sigma_t$, $\gamma_x$ and $\gamma_y$ parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters. 108

6.7 Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same $\sigma_r$, $\sigma_t$, $\gamma_x$ and $\gamma_y$ parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters. 109

6.8 Example datasets from fits of the time dependent data analysis. For every single dataset, all peaks have the same $\sigma_r$, $\sigma_t$, $\gamma_x$ and $\gamma_y$ parameters. The fit model describes the shape nicely in dependence of the time with only 9 free parameters. 110

6.9 Sketch of the four stages of the droplet drying. The insets show the corresponding pictures of the microscope camera, which are in good agreement. 112

6.10 Integrated intensity of the peak and incoherent background versus time in comparison to the height of the droplet measured by the LBM. The four stages of the mesocrystal growth independently observed with the LBM are indicated by the colored regions for the measurement with medium evaporation time (pale colors) and by the gray lines for the short evaporation time (strong colors). The value $t_0$ describes the starting time of the nucleation. Each intensity point is the result of the GISAXS data treatment of one measurement described in section 5.3.2. 114

6.11 Comparison of structural parameters versus time. Due to necessary available ordered system for this investigation, only the last two stages are indicated by the colored rectangular in the background for the medium measurement (pale colors) and by the gray lines for the short evaporation time (strong colors). The value $t_0$ describes the starting time of the nucleation. The black line indicates a perfect closed packed lattice, which will be crossed for every sample. 114

7.1 Description of the extraction process of a single mesocrystal (highlighted in color). 120

7.2 Single mesocrystal sample as used. 120

7.3 High resolution diffractometer P08 at Petra III. 123

7.4 Sketch of the used cmesh. 123

7.5 Mesocrystal view in the beam direction. 125
7.6 Diffraction pattern from a single mesocrystal with cubic building blocks for different reciprocal planes. A simulation of these patterns is shown in the appendix section A.3.3. ................................................................. 126

7.7 Diffraction pattern from a single mesocrystal with spherical building blocks for different reciprocal lattice planes. ................................................................. 127

7.8 Measurement of the (h0l) plane from MC shows the presence of twin domains. Each color indicates peaks, which belong to one twin. A TEM picture on the left side visualizes the existence of such twins in a single mesocrystal again colored in dependence of the orientation. This microscope picture was measured on a mesocrystal of the same sample. The zoom shows the splitting of one of the peaks suggesting several crystallites with slightly different lattice constants. ... 130

7.9 Measurement of the (h0l) plane of a single mesocrystal with cubic particles. The zoom around the (002) reflection shows nice Laue oscillations, which could be reproduced with a simulation. The left inset shows a vertical line scan through the reflection. ................................................................. 132

7.10 Cross-section through the reflexes (101) and (101) in Q direction from figure 7.9a. The Laue oscillations are fitted with a Laue function in combination with a form factor, a particle size and lattice constant distribution and an incoherent background. The influence of a larger lattice constant distribution (σcMC) and height distribution (σNL) is shown in figure 7.10b. ................................................................. 133

7.12 Rocking scans for different peaks of the (h0l) plane of MC. The grey line is the form factor of a perfect mesocrystal with defined sizes by SEM and shows the natural line shape. The filled curves shows a Lorentz function with HWHM determined at the Qy-Qz plots, presenting the natural line shape of the present mesocrystal with limited correlation length. FMC(θ) is the perfect mesocrystal form factor. ................................................................. 135

7.11 Definition of the regions for the integration and a background. ................................................................. 135

7.13 Sketch of different mosacity components. The rotation vector is in the viewing direction. ................................................................. 137

7.14 SEM pictures from top of mesocrystals of equivalent samples. ................................................................. 138

7.15 Integrated intensities of MC. ................................................................. 139

7.16 Results of fits from the truncated cube and the rounded cube model. Figure 7.16a and 7.16b fitted for a perfect cube and figure 7.16e and 7.16f for a perfect spherical particle shows the correctness of the new rounded cube model. The best parameters for the respective models are shown in figure 7.16c and 7.16d. 141

7.17 Real space representation of the rounded and truncated cube model with the best fitting truncation parameters. ................................................................. 143

A.1 Illustration of characteristics of the mesocrystal self-assembling. ................................................................. 151

A.2 Illustration of characteristics of the mesocrystal self-assembling. ................................................................. 152

A.3 SEM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up. The SEM picture is made from top of a mesocrystal. ................................................................. 152

A.4 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up. ................................................................. 153

A.5 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up. ................................................................. 154
Appendix D List of Figures

A.6 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up. 155
A.7 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up. 156
A.8 SEM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under different field conditions. 157
A.9 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient in-plane configuration. 158
A.10 AFM characterization of an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient in-plane configuration. 159
A.11 Ensemble of mesocrystals formed from spherical building blocks self-assembled with different evaporation times for a gradient in-plane configuration. 160
A.12 Diffraction pattern from single mesocrystals with cubic or spherical building blocks for different crystalline planes. 164
A.13 Diffraction pattern from single mesocrystals with cubic building blocks for different crystalline planes. 165
A.14 Calculated diffraction pattern from single mesocrystals with cubic building blocks for the (h0l) plane. The influence of the Lorentz factor is shown by comparison of simulations with and without consideration. 168
A.15 Calculated diffraction pattern from single mesocrystals with cubic building blocks for the (hhl) plane. The influence of the Lorentz factor is shown by comparison of simulations with and without consideration. 169
A.16 Rocking scans for different peaks of the (HOL) plane of $M_{C}$ in Q space. The peak width are obviously very similar, showing a small influence of the mosaicity on the measured shape. 170
A.17 Translation scans of the (100) and (001) reflections to measure the homogeneity/inhomogeneity of the beam. The curves with dark color are scans over the beam height and show sharp peaks which indicate a small beam. The lighter color plots are scans over the beam width, which show a large and inhomogeneous beam in this direction. 170
A.18 Results of fits from the truncated cube model. Figure A.18a fitted for a perfect cube and figure A.18f for a cubeoctaedron. The best parameters for the respective models are shown in figure A.18e. 174
A.19 Results of fits from the rounded cube model. Figure A.19a fitted for a perfect cube and figure A.19f for a perfect spherical particle. The best parameters for the respective models are shown in figure A.19d. 175
# Appendix E

## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Produced nanoparticle solutions which were used.</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>Results of the SAXS analysis for the morphological characterization of spherical and cubic $\gamma$-$Fe_2O_3$ particles. The data for the cubes were fitted with different form factor (FF) models as comparison. The description of the models can be found in section 5.1.1. The errors are estimated from the fitting procedure.</td>
<td>44</td>
</tr>
<tr>
<td>4.3</td>
<td>Results of the structural analysis of the ensemble of mesocrystals formed with long/extra long waiting time from spherical/cubic building blocks of radius 5.01 nm/edge length 10.9 nm and degree of truncation of 0.8 self-assembled under an magnetic field of 80 mT and gradient up/without a magnetic field. These outcomes are an average over the ensemble of mesocrystals.</td>
<td>59</td>
</tr>
<tr>
<td>4.4</td>
<td>Results from the systematic investigation of the field influence on the outcome of the mesocrystals growth. Microscopy as well as depth resolved GISAXS experiments reveal different characteristics and the combination leads to a good description of the quality of the sample. The parameters $\varepsilon_{y/z}$ are the the average mesocrystal in-plane/out-of-plane correlation length and $\sigma_{rad/tilt}$ the radial/tangential standard deviations describing a random variation of the mesocrystal lattice parameters and tilting of the $c$-axis away from the substrate surface. The large error values for the in-plane correlation lengths result from approaching the instrumental resolution limit. (*: Measurement from a comparable sample.)</td>
<td>68</td>
</tr>
<tr>
<td>5.1</td>
<td>Fit parameters used for the simulation shown in figure 5.8.</td>
<td>97</td>
</tr>
<tr>
<td>5.2</td>
<td>Fit parameter used for the simulation shown in figure 5.9b.</td>
<td>99</td>
</tr>
<tr>
<td>6.1</td>
<td>Sample parameters which were used for the ESRF in-situ experiment.</td>
<td>104</td>
</tr>
<tr>
<td>6.2</td>
<td>Received values from the LBM, camera and 3D GISAXS pattern. Duration$<em>{zero}$ shows the time until the LBM value is zero. Duration$</em>{nuc}$ is the value for the nucleation, which is read out the 3D GISAXS pattern. The errors for the time values read out from the camera is 0.5 min, for the LBM 0.1 min and from the GISAXS pattern 0.5 min.</td>
<td>111</td>
</tr>
<tr>
<td>7.1</td>
<td>Produced mesocrystals which were used for the diffraction experiment and their main parameters.</td>
<td>121</td>
</tr>
</tbody>
</table>
7.2 Lattice constant and correlations length taken from the average of reflexes from different planes of the single mesocrystal measurements. For $\text{M}_I$ the (h0l) plane was used. Due to asymmetric peak shapes and unknown factors as e.g. influence of the measurement method on the peak shape, the width are expected to be increased. The different colors red and cyan belong each to one twin according to figure 7.8. The three grains with the same orientation, enumerated in the scattering image figure figure 7.8, have been treated separately to derive the data shown and are color coded here as 1, 2 and 3. For a comparison the lattice constant values for an average over an ensemble of mesocrystals are shown below the line.

7.3 Result of the Laue oscillation fit from the (101) reflection.

7.4 Width of the rocking scan peaks measured on $\text{M}_C$ determined by numeric calculation of the standard deviation.

7.5 Result of the rocking scan analysis for mosaicity. The a-axis component is determined from the (00l) reflexes and the c-axis component from the (10T) reflexes, both from the (h0l) plane.

7.6 Fit parameters of the models shown in figure 7.15b. The parameters without error have not been fitted, errors with NaN denote numerical problems in the error calculation.

A.1 Example fit parameters of the time-resolved in-situ GISAXS study. The errors are small as they are only numerical results from the fitting algorithm.

A.2 Lattice constants and correlation lengths taken from reflexes of different reciprocal lattice planes of the single mesocrystal measurements. The values are averages of two individual peaks at positions mirrored at the origin to remove any effect from an imperfect determined zero position. Reflexes with two well separated peaks have two values, one for each individual peak.

A.3 Integrated intensities of symmetry equivalent reflexes of (002) at a Q position of 0.083 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

A.4 Integrated intensities of symmetry equivalent reflexes of (004) at a Q position of 0.165 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

A.5 Integrated intensities of symmetry equivalent reflexes of (101) at a Q position of 0.062 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

A.6 Integrated intensities of symmetry equivalent reflexes of (110) at a Q position of 0.066 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

A.7 Integrated intensities of symmetry equivalent reflexes of (112) at a Q position of 0.106 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.

A.8 Integrated intensities of symmetry equivalent reflexes of (121) at a Q position of 0.112 from $\text{M}_I$. I are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a.
A.9 Integrated intensities of symmetry equivalent reflexes of (200) at a Q position of 0.093 from $M'_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a. 172

A.10 Integrated intensities of symmetry equivalent reflexes of (202) at a Q position of 0.125 from $M'_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a. 173

A.11 Integrated intensities of symmetry equivalent reflexes of (220) at a Q position of 0.132 from $M'_C$. $I$ are the uncorrected and $I_L$ are the Lorentz corrected integrated intensities, which are shown in figure 7.15a. 173

A.12 Average of the integrated intensities of symmetry equivalent reflexes from $M'_C$. $\langle I_{\text{exp}} \rangle$ are the measured integrated intensities, Lorentz corrected and averaged and $I_{\text{calc,rounded}}$ are the simulated intensities of the rounded cube model. Both are shown in figure 7.15b. $R_{\text{int}}$ and $R_1$ are the R factors known from crystallography, which quantify the quality of the data and the goodness of the fit, respectively. ($R_1$-rounded cubes: 18%, $R_1$-truncated cubes: 21%, $R_1$-spheres: 13%) 173
Appendix F

List of Symbols, Abbreviations and Definitions

F.1 Symbols

**Mathematic Symbols**
- $\delta$ \hspace{1cm} delta-distribution
- $\partial$ \hspace{1cm} partial derivative
- $\Delta x$ \hspace{1cm} difference of $x_2 - x_1$
- $\vec{v}$ \hspace{1cm} vector
- $\hat{e}_v$ \hspace{1cm} unit vector parallel to $\vec{v}$
- $a \otimes b$ \hspace{1cm} convolution of $a$ and $b$
- $\mathcal{F}(f)$ \hspace{1cm} Fourier transform of function $f$
- $\mathcal{F}^{-1}(F)$ \hspace{1cm} Fourier back transform

**Physical Nomenclature**
- $a$ \hspace{1cm} average in-plane lattice constant of the nanoparticle superstructure from an ensemble of mesocrystals
- $A$ \hspace{1cm} magnetic exchange constant
- $a_{DW}$ \hspace{1cm} mean squared displacement of the lattice position by the Debye-Waller factor term
- $a_{NP}$ \hspace{1cm} edge length of a cubic nanoparticle
- $c$ \hspace{1cm} average out-of-plane lattice constant of the nanoparticle superstructure from an ensemble of mesocrystals
Appendix F List of Symbols, Abbreviations and Definitions

**Physical Nomenclature (continued)**

- $D$ diffusion coefficient
- $f(\vec{Q})$ atomic form factor
- $F_{\text{Shape}}(\vec{Q})$ nanoparticle form factor for different shapes (spheres, T-Cubes or R-Cubes)
- $H_\perp$ low magnetic field with field gradient pointing away from the substrate
- $H_\parallel$ low magnetic field with field gradient pointing to the substrate
- $H_\perp$ low magnetic field with field gradient pointing in an in-plane direction of the substrate
- $H_\perp$ strong magnetic field with field gradient pointing away from the substrate
- $H_\parallel$ strong magnetic field with field gradient pointing to the substrate
- $H_\perp$ strong magnetic field with field gradient pointing in an in-plane direction of the substrate
- $h$ height of the droplet measured by the light-band micrometer
- $H$ external applied field
- $hkl$ Miller indices
- $H_\Rightarrow$ homogeneous magnetic field in in-plane direction to the substrate
- $H_\Rightarrow$ homogeneous magnetic field in out-of-plane direction to the substrate
- $I$ measured scattering intensity
- $K$ uniaxial anisotropy constant
- $\vec{k}_{i/f}$ incident and outgoing wave vector with $k = \frac{2\pi}{\lambda}$
- $k_B$ Boltzmann constant
- $L(\chi)$ Langevin function
- $m$ magnetic moment of a nanoparticle
- $M(H)$ average magnetic moment of a sample
- $M_s$ saturation magnetization
- $n$ natural number $\mathbb{N}$, refractive index
- $N_A$ Avogadro constant $(6,02214129 \cdot 10^{23} \text{ mol}^{-1})$
- $N_l$ number of repetitions of the unit cell by a Laue function
- $N_{\text{NP}}$ number of nanoparticles in the sample
- $P_{\text{MC}}$ parameter determined from the single mesocrystal diffraction experiment
- $\vec{Q} = \vec{k}_f - \vec{k}_i$ scattering vector
- $Q_{x/y/z}$ $x/y/z$ component of the scattering vector
- $R$ ideal gas constant $(= N_A \cdot k_B = 8.3144621 \text{ J mol}^{-1} \text{ K}^{-1})$
- $\vec{r}$ real space vector
- $r_c$ critical radius below particles act as a single domain particle
- $r_e$ classical electron radius $(2.81 \cdot 10^{-15} \text{ m})$
- $r_{\text{NP}}$ average radius of a spherical nanoparticle determined from a solution by SAXS
- $r_{\text{shell}}$ average radius of the organic shell thickness determined from a solution by SAXS and SANS
- $S(\vec{Q})$ structure factor
- $t$ time
- $T$ temperature
**Physical Nomenclature** (continued)

- $T_B$: blocking temperature
- $t_0$: starting time of the nucleation
- $V$: particle volume
- $V(\vec{r})$: scattering potential
- $x_{MC}$: parameter $x$ measured at a single mesocrystal (MC)
- $\alpha_{i/f/c}$: incident/outgoing/critical angle
- $\gamma$: half-width at half-maximum (HWHM) of the Lorentz function, natural linewidth of an ensemble of mesocrystals
- $\gamma_{y/z}$: in-plane/out-of-plane mesocrystal half-width at half-maximum
- $\varepsilon_{y/z}$: in-plane/out-of-plane mesocrystal correlation length averaged over the ensemble statistic
- $\eta$: friction coefficient
- $\lambda$: wavelength
- $\mu$: absorption length
- $\mu_0$: vacuum permeability
- $\rho$: density
- $\sigma$: depending on context: standard deviation describing a Gaussian distributed variation or scattering cross-section
- $\sigma_{\text{NP/rNP}}$: standard deviation describing a Gaussian distributed variation of the edge length of a cubic/ radius of a spherical nanoparticle
- $\sigma_{\text{MC}}$: standard deviation describing a Gaussian distributed variation of the lattice parameter $c$ in a single mesocrystal
- $\sigma_{N_L}$: standard deviation describing a Gaussian distributed variation of the number of repetitions of the unit cell in one mesocrystal
- $\sigma_{r/t}$: standard deviation describing a random variation of the mesocrystal lattice parameters/ a Gaussian distributed tilting of the $c$-axis away from the substrate surface (ensemble of mesocrystals)
- $\tau$: degree of truncation
- $\tau_0$: characteristic attempt time
- $\tau_m$: time scale of the experiment
- $\tau_N$: Néel relaxation time
- $\tau_{\text{Round/Trunc}}$: degree of truncation for the rounded/truncated cube model
- $[uvw]$: specific direction in a lattice
- $(hkl)$: specific plane in a lattice
- $\langle x \rangle$: mean value $x$
- $\Psi$: wave function
### Sample Emblems

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^S_M$</td>
<td>single mesocrystal with spherical building blocks</td>
</tr>
<tr>
<td>$M^C_M$</td>
<td>single mesocrystal with cubic building blocks</td>
</tr>
<tr>
<td>$S^S_{8.4}$</td>
<td>nanoparticle solution of spheres with a concentration of $8.4 \cdot 10^{14}$ NP/ml</td>
</tr>
<tr>
<td>$S^C_{8.4}$</td>
<td>nanoparticle solution of cubes with a concentration of $8.4 \cdot 10^{14}$ NP/ml</td>
</tr>
<tr>
<td>$D^{Lg1.68,80}_{S,5.01}$</td>
<td>example for a sample with an ensemble of mesocrystals formed from spherical building blocks self-assembled under a magnetic field of 80 mT and gradient up</td>
</tr>
</tbody>
</table>

### F.2 Abbreviations

#### Instruments

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D8</td>
<td>Bruker laboratory x-ray reflectometer (in house)</td>
</tr>
<tr>
<td>ID01</td>
<td>X-ray diffraction and scattering beamline for coherent x-ray diffraction, SAXS and GISAXS experiments at the ESRF synchrotron in Grenoble, France</td>
</tr>
<tr>
<td>MARIA</td>
<td>Magnetic reflectometer with high incident angle for polarized neutron reflectometry and GISANS at the MLZ neutron center in Garching, Germany</td>
</tr>
<tr>
<td>P08</td>
<td>High resolution diffraction beamline at the PETRAIII synchrotron in Hamburg, Germany</td>
</tr>
<tr>
<td>SWING</td>
<td>X-ray diffraction and scattering beamline for SAXS and GISAXS experiments at the SOLEIL synchrotron in Saclay, France</td>
</tr>
<tr>
<td>4-circle</td>
<td>Huber laboratory 4-circle diffractometer (in house)</td>
</tr>
</tbody>
</table>

#### Methods

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>GISANS</td>
<td>Grazing incidence small angle neutron scattering</td>
</tr>
<tr>
<td>GISAXS</td>
<td>Grazing incidence small angle x-ray scattering</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle x-ray scattering</td>
</tr>
<tr>
<td>SEAD</td>
<td>Selected area (electron) diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray reflectometry</td>
</tr>
</tbody>
</table>
### Materials

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>cobalt</td>
</tr>
<tr>
<td>Cu</td>
<td>copper</td>
</tr>
<tr>
<td>Fe</td>
<td>iron</td>
</tr>
<tr>
<td>NaI</td>
<td>sodium iodide</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>Si</td>
<td>silicon</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>Maghemite</td>
</tr>
</tbody>
</table>

### Abbreviations for theory

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>Born Approximation</td>
</tr>
<tr>
<td>DWBA</td>
<td>distorted wave Born approximation</td>
</tr>
<tr>
<td>FF</td>
<td>form factor</td>
</tr>
<tr>
<td>SF</td>
<td>structure factor</td>
</tr>
<tr>
<td>SLD</td>
<td>scattering length density</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
</tbody>
</table>

### General abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>bct</td>
<td>body-centered tetragonal</td>
</tr>
<tr>
<td>BG</td>
<td>background</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electrons</td>
</tr>
<tr>
<td>ETD</td>
<td>Everhart Thornley detector</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close-packed</td>
</tr>
<tr>
<td>HWHM</td>
<td>half-width at half maximum</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>LBM</td>
<td>light-band micrometer</td>
</tr>
<tr>
<td>MC</td>
<td>single mesocrystal</td>
</tr>
<tr>
<td>Nₜ</td>
<td>number of repetitions of the unit cell/oscillations for the Laue function</td>
</tr>
<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>SD</td>
<td>standard deviation</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electrons</td>
</tr>
<tr>
<td>TLD</td>
<td>through the lens detector</td>
</tr>
<tr>
<td>TPCL</td>
<td>triple phase contact line</td>
</tr>
<tr>
<td>vCD</td>
<td>low-voltage high-contrast solid state detector</td>
</tr>
</tbody>
</table>
F.3 Definitions

- **truncation**: general term for "truncation" of the edges by cubic particles
- **nanocrystal**: other word for single crystalline nanoparticle
- **nanoparticle structure**: atomic crystal structure of one single nanoparticle
- **mesocrystal**: 3 dimensionally highly ordered ensemble of nanoparticles
- **mesocrystal structure**: supercrystal structure or nanoparticle superstructure inside one mesocrystal
- **rounded**: spherical truncation by cubic particles
- **single mesocrystal**: one mesocrystal isolated from an ensemble of mesocrystals
- **truncated**: flat truncation by cubic particles
- **2D powder**: sample with arbitrary orientated in-plane crystals, but with a preferred c-direction
Ganz zum Schluss möchte ich mich ganz herzlich bei allen Leuten bedanken, die mich im Laufe der Dissertation begleitet, in jeder Hinsicht tatkräftig unterstützt und ohne die eine solche Arbeit gar nicht möglich gewesen wäre.

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Elisabeth Josten

Member of the Helmholtz Association