Self-assembly of magnetic particles

HAUKE CARSTENSEN
Abstract

Self-assembly is the spontaneous formation of larger structures from small building blocks. This process is driven and determined by the interactions between the constituents. Examples of self assembly are found almost everywhere and, in particular, biological systems in general rely on a hierarchical formation of structures over a range of length scales. Technologically, self-assembly can be used to form mesoscopic structures and artificial crystals. In the case of particles with micrometer size suspended in a liquid phase, it is possible to use optical microscopy for the investigation of self-assembly.

In this thesis, the self-assembly of microbeads with tunable magnetic interactions is studied, based on the statistic analysis of microscope images and computer simulations. Magnetic and non-magnetic microbeads are suspended in a ferrofluid, which is a dispersion of magnetic nanoparticles in water. As a result, the magnetic properties of the microbeads in the ferrofluid are altered and can be described by effective magnetic susceptibilities and magnetic dipole moments, which can be tuned continuously. The liquid is confined between glass slides and effectively the microbeads are studied in a 2D geometry under a magnetic field, applied either in- or out-of-plane. The resulting structures are detected by image analysis algorithms, analyzed and correlated to the dipolar interaction between the beads, as well as to macroscopic quantities, like the particle density and ratio. For the in-plane field a phase transition from square to hexagonal lattice is observed. This phase transition is explained by the change in dipole interaction between the microbeads as the moments change from anti-parallel to parallel alignment. For the out-of-plane field the situation becomes diverse and more phases appear. It turns out that the phase formation in this case is strongly dependent on the bead ratio, density and interactions.

We identify regions in the phase diagram, where isolated beads, percolated structures, and crystals dominate. To cover a wide parameter range the experiments are complemented by computer simulations. The tools developed in this thesis enable us to construct phase diagrams extracted from direct imaging and dependence on the extracted relevant parameters.

Keywords: self-assembly, tunable interactions, phase transition, ferrofluid

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List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  Phase formation in colloidal systems with tunable interaction
   H.Carstensen, V. Kapaklis, M. Wolff.

II  Statistical analysis of colloidal phase formation
    H.Carstensen, V. Kapaklis, M. Wolff.

III Tunable self assembly of crystals and branching chain networks
    Manuscript

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My contributions to the papers:

I Designed the experiment, participated in the sample preparations and measurements, analyzed the data and responsible for writing the majority of the manuscript

II Automated the experiment, performed sample preparations and measurements, analyzed the data and responsible for writing the majority of the manuscript

III Wrote the code for the simulation, analyzed the data, and responsible for writing the majority of the manuscript

The following paper is not included in this thesis:

1. Free directional printing of biopolymer hydrogel based on dynamic metal ion-chelating ligand coordination bonds

The following patent is based on the results presented in this thesis:

1. Electrical device with low friction contact parts
   H. Carstensen, B. Hjörvarsson, M. Wolff, V. Kapaklis
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1. Introduction

Self-assembly is the formation of structure from building blocks driven by their interactions. In this sense, it describes the formation of matter on all length scales from hadrons [1] to galaxies [2]. One important field is biology and one of the most exciting questions of science, the origin of life, is explained by the self-assembly of molecules [3].

In a more narrow sense, the term can be distinguished from the general formation of structure by limiting it to "processes that involve pre-existing components [...] are reversible, and can be controlled by proper design of the components" [4]. A distinguished system for the study of self-assembly are colloids. Colloids are particles dispersed in liquid and are encountered in everyday life. One example is paint consisting of nanoparticles dispersed in oil or water. Colloidal particles that are at a length scale much larger than the wavelength of light can be observed by light microscopy. They are interesting to study, because of the great variety of interactions and building blocks that can be realized. Examples for interactions are electrical [5, 6], magnetic [7, 8, 9, 10, 11], and key-lock [12]. The building blocks can have shapes such as spheres [13, 14, 15, 16], cubes [17], rods [18] or even more complex ones [19].

Colloids can self-assemble structures similar to atoms, such as colloidal crystals and can be used as a model system [20]. An important factor is the ratio of thermal energy to interaction potentials between the colloidal particles. If this ratio is high enough, the particles are in dispersion. An example is a ferrofluid, magnetic nanoparticles dispersed in liquid. At an intermediate thermal energy, the particles can self-assemble low energy configurations, such as colloidal crystals. If the thermal energy is low compared to the interaction potential, the lowest energy configuration is not always reached, but a disordered structure is assembled. One example are magneto-rheological fluids [21], where suspended magnetic particles form chains, when a magnetic field is applied. The chains are not the lowest energy configuration, but are stable for a long time, sufficient for technical applications. The chain formation can lead to a drastically increased viscosity, making the fluid effectively solid, a phenomena that is used e.g. in magnetically tunable shock absorbers [22].

It was the first time reported in 1984 by A.T. Skjeltorp that non-magnetic particles suspended in ferrofluid display an effective magnetic behavior and form ordered structures [23]. Since then, the principle has been studied in
many different systems [24, 25, 26], with binary colloids [27, 28, 29, 30] or with templated surfaces [31]. Khalil et al. [28] have discovered a variety of phases in a binary magnetic colloidal system.

In this thesis, the behavior of microbeads in ferrofluid is studied. The system is similar to the previously mentioned binary colloids, but extends the investigations to larger beads and different dynamics. As a result, meta-stable structures, e.g. branching chains, have been found. The microbead interactions can be tuned by varying the ferrofluid susceptibility and, as a result, a variety of phases has been observed. Image analysis is used to extract order parameter in order to quantify the transition between phases.

The thesis is introduced by providing the basic physics and a theoretical background and the the experimental methods. The results that are published in the papers are presented and discussed.
2. Theoretical background

Colloidal self-assembly is determined by the interactions between the building blocks. Depending on the thermodynamics and the energy landscape the process results in a stable or meta-stable equilibrium configuration. In this chapter, the thermodynamics, phases, and tunable magnetic and relevant non-magnetic interactions are introduced.

2.1 Thermodynamics

2.1.1 Phase formation

Self-assembly is the formation of phases driven by the interaction of building blocks, where a phase is "a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system" [32]. Phase formation may start from an unstable configuration and result in an equilibrium state. The equilibrium is called stable, if it is the state with the global minimum in the Gibbs free energy or meta-stable if it is a local minimum. Gibbs free energy is defined as [33]

$$ G = H - TS $$

$$ = E + pV - TS, $$

where $H$ is the enthalpy, $E$ the inner energy, $p$ the pressure, $V$ the volume, $T$ the temperature, and $S$ the entropy. Condensed matter, solid or liquid, is usually assumed to be incompressible [32], so that the volume term can be dropped. Furthermore, for large building blocks, $TS$ can be small compared to $E$, in which case Gibbs free energy is just the inner energy $G \approx E$. An example is macroscopic permanent magnetic dipoles, which can be assembled into different (meta-)stable configurations as shown in fig. 2.1. The figure shows two configurations with energy minima seperated by an energy barrier. The ring configuration can be transformed into the square configuration by pushing two opposite sides together. However, the transitional states have a higher energy with a maximum, the energy barrier, $E_B$. The energy required to overcome the barrier is $\Delta E_{r-b}$ from the ring configuration to the lattice and $E_{s-b}$ for the reversed direction. An example for atoms, is carbon with graphite as the global energy minimum configuration and diamond as a meta-stable state.

A crystalline phase is formed when atoms arrange themselves in a periodically, which is in most cases the lowest energy state. On the atomic level
crystals are formed in most solid materials, e.g., in ice and in metals. Particles in colloids can also form ordered structures called colloidal crystals, an example is shown in fig. 2.2.

In thermal equilibrium the distribution of occupied states with energies $E_i$ is described by the Boltzmann distribution [34]

$$p_i \propto e^{-\frac{E_i}{k_B T}}, \quad (2.3)$$

where $k_B$ is the Boltzmann constant. The Boltzmann distribution holds for atomic systems (over accessible energy states). For larger building blocks such as colloidal particles, the thermal energy can be small compared to the energy barriers between the equilibrium states. The rate at which energy barriers are passed is described by the Arrhenius’ equation and is proportional to the Boltzmann factor

$$k \propto e^{-\frac{E_{LM} - E_B}{k_B T}}, \quad (2.4)$$

where $E_{LM}$ is the local minimum energy and $E_B$ is the height of the energy barrier (see fig. 2.1). The Boltzmann factor defines the probability that a system can reach a global energy minimum state.

If the thermal energy is much lower than the interaction potentials, the system will not assemble in the stable equilibrium configuration (e.g., a crystal), but will remain in a meta-stable phase. Furthermore, the lowest energy config-

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**Figure 2.1.** Schematic illustration of the energy landscape for magnetic dipoles. Magnetic disks with permanent in-plane moment can be configured in a variety of (meta-)stable configurations such as in a chain, ring, square, or hexagonal lattice. A ring with energy $E_r$ can be transformed into a square lattice with $E_s$ by pushing two opposite side together.
uration is not always reached, if the particle motion is very slow. If the particle motion asymptotically approaches zero, the structure is dynamically arrested.

A ferrofluid is an example, where the thermal energy is larger than the magnetic interaction potential between particles. In this case, energetically higher states are occupied and the magnetic interaction does not stabilize particle agglomerates. The nanoparticles are randomly distributed in the liquid and stay in dispersion even with an externally applied magnetic field. This is not the case for magnetic microbeads, which form chains and cluster if a field is applied. The change from dispersed to the flocculated state is used in magnetorheological fluids. Magnetorheological fluids and ferrofluids differ in the size of the dispersed particles. Whether magnetic particles flocculate or remain dispersed, when an external field is applied, can be calculated theoretically [35], but depends on the exact knowledge of the colloidal properties.

In the case of superparamagnetic particles, the interaction potential is zero until an external field is applied, so that the particles are random distributed, corresponding to a high temperature Boltzmann distribution. After a field is applied, the thermal energy is small compared to the interaction potential and the Boltzmann factor drops immediately. The same happens, if (with constant interaction potential) the temperature would be reduced rapidly. The process of rapid cooling is called quenching and can cause the system to remain in a meta-stable state.
2.1.2 Entropy
Entropy can be defined differently depending on the context, but a common definition is

\[ S = k_B \ln \Omega, \]  

(2.5)

where \( \Omega \) is the number of microscopic states (configurations) that represent the same macroscopic phase. An example with high entropy is a gas, where the gas molecules are randomly distributed. Even when all macroscopic variables (such as pressure) are constant, the exact configuration of the molecules is different at each single point in time, because of the Brownian motion. However, at a macroscopic level, all configurations represent the same phase. On the other hand, a perfect crystal (without degeneration) has zero entropy, because the building blocks are constraint into a single configuration. In an isolated system, entropy is always increasing over time.

2.2 Tunable magnetic interactions
The self-assembly is driven by magnetic interactions between the microbeads based on the effective susceptibilities that the suspended beads in ferrofluid display. The effective moments are derived and magnetic interactions are approximated as dipole-dipole interactions. The interactions are described for in-plane and out-of-plane external magnetic fields.

2.2.1 Dipole interactions
The driving force for the self-assembly of microbeads in ferrofluid is the magnetic dipole force between the beads. The dipole interaction depends on the angles of the moments of the particles with respect to the connecting line as shown in fig. 2.3. The potential energy between two point dipoles with the magnetic moments \( m_1 \) and \( m_2 \) is

\[ U = -\frac{\mu_0}{4\pi} \frac{m_1 m_2}{r^3} \cdot (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2), \]  

(2.6)

where \( r \) is the distance between the dipoles and the angles are defined as in fig. 2.3.
In-plane field

If an external field of a few millitesla is applied, the magnetic moments of the beads align with respect to the external field as shown in fig. 2.4. The interactions for an applied in-plane field are anisotropic and the magnetic potential energy with both dipoles aligned to the external field ($\theta_1 = \theta_2 = \theta$) is

$$U_{\text{in}} = -\frac{\mu_0}{4\pi} \cdot \frac{m_1 m_2}{r^3} \cdot 3 \left( \cos \theta^2 - \frac{1}{3} \right). \quad (2.7)$$

The magnetic potential energy for dipoles that are in a row along the external field ($\theta_1 = \theta_2 = 0^\circ$) is

$$U_{\theta=0^\circ} = -\frac{\mu_0}{2\pi} \cdot \frac{m_1 m_2}{r^3}. \quad (2.8)$$

If the dipoles are in a row perpendicular the external field, the magnetic potential energy ($\theta_1 = \theta_2 = 90^\circ$) is

$$U_{\theta=90^\circ} = \frac{\mu_0}{4\pi} \cdot \frac{m_1 m_2}{r^3}. \quad (2.9)$$

The potential of beads that are in a line along to the external field is twice as strong as the potential of beads that are in a line perpendicular to the external field. Furthermore, the sign of the magnetic potential is different. Two beads with parallel moments that are in a line parallel to the external field attract each other and two beads in a perpendicular line repulse each other. If their moments are anti-parallel with respect to each other, attraction and repulsion are exchanged as compared to the case of parallel moments.

Out-of plane field

In an out-of-plane field the magnetic potential energy is

$$U_{\text{out}} = \frac{\mu_0}{4\pi} \cdot \frac{m_1 m_2}{r^3}. \quad (2.10)$$
The dipoles are in a plane perpendicular to the field lines (as shown in fig.2.5) \( (\theta_1 = \theta_2 = 90^\circ) \). The interactions are isotropic and the phase formation is mainly determined by the competition of attractive and repulsive interactions. The interaction is repulsive between two beads with parallel moments and attractive between two beads with anti-parallel moments. This is the same potential as for beads that are in a row perpendicular to the applied in-plane field.

2.2.2 Magnetic materials

The magnetic properties of a material can be characterized by the response of the material to an external magnetic field. An important measure is the magnetic susceptibility, which is defined as the ratio of the magnetic moment \( m \) of a material to the applied field \( H \),

\[
\chi = \frac{m}{H}.
\]  

The following types of magnetic response can be distinguished:

<table>
<thead>
<tr>
<th>Type</th>
<th>( \chi ) (typical)</th>
<th>Remanence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>( 10^{-5} ) [36]</td>
<td>no</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>( 10^{-5} - 10^{-2} ) [36]</td>
<td>no</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>( 10^2 - 10^6 ) [36]</td>
<td>yes</td>
</tr>
<tr>
<td>Superparamagnetism</td>
<td>-</td>
<td>no</td>
</tr>
</tbody>
</table>

Diamagnetism is a magnetic response, where the material has a negative magnetic susceptibility and an induced magnetic moment anti-parallel to the applied field. Every material is diamagnetic, but the effect is generally small, so that materials with no other form of magnetic response are often called non-magnetic.
Paramagnetic materials have a positive magnetic susceptibility, so that their magnetic moment is parallel to the applied field. Such materials contain magnetic atoms that are spatially separated from each other and that are not interacting with each other. The orientation of the individual magnetic moments is Boltzmann distributed. Without an external field, the magnetostatic energy is zero and the magnetic moments are randomly oriented. With an applied field, the moments align to the external field and the magnetic response can be described by the Langevin function, which can be derived from the Boltzmann distribution [36].

Ferromagnetic materials have a positive susceptibility, but have a more complex magnetic behavior. They consist of permanently magnetized domains even without an externally applied field. Every domain has a magnetic moment. The moments of the domains can be randomly oriented and cancel each other out or aligned to each other and add up at a macroscopic length scale. A ferromagnetic material has a positive magnetic susceptibility, since the moments of the magnetic domains align with the external field and domains parallel to the external field increase in size as the field strength increases. At the saturation field strength, the domains are as much aligned as possible for the given material.

Superparamagnetism exhibits a response similar to paramagnetism but with a much higher susceptibility. The superparamagnetic materials consist of ferromagnetic domains with some degree of rotational freedom. An example for a superparamagnetic material is a ferrofluid, which is a dispersion of magnetic nanoparticles in a liquid. Each nanoparticle consist of a single permanently magnetic domain. Without an applied field, the magnetic moments of the nanoparticles are random oriented and cancel each other out. If an external field is applied, they align with the field, and the magnetic moments sum up at larger length scales. The difference to paramagnetism is that the magnetic units have much higher magnetic moments, since they contain a large number of magnetic atoms. Therefore, the Boltzmann distribution is different and the magnetic domains align more with respect to the external field than the individual atoms in the case of a paramagnetic material.

2.2.3 Effective Susceptibility

The interaction between beads dispersed in a magnetic liquid can be tuned by changing the susceptibility of the surrounding medium. Two types of beads, magnetic and non-magnetic, are used in our experiments. They are on the micrometer length scale and have a spherical shape. On the length scale of the microbeads the ferrofluid can be described as a continuous magnetic medium, because the nanoparticles in the ferrofluid are several orders of magnitude smaller than the microbeads.
Instead of describing the system as (magnetic) spheres in a magnetic medium it can be viewed as magnetic spheres in vacuum with altered magnetic susceptibility, which can be called effective magnetic susceptibility. The magnetic susceptibility as defined in eq. 2.11 applies for an infinitely large volume, but for a real object the geometry has to be taken into account. The induced magnetic moment creates a magnetic field itself, the so called demagnetization field. Therefore, the induced magnetic moment of an object is shape dependent. The micro beads can be well approximated as spheres. From the boundary conditions and continuity of the magnetic potential and field strength [37] the following equation can be derived where

\[ H_1 = H_0 - Aa^{-3}, \quad (2.12) \]

\[ \mu_1 H_1 = \mu_2 (H_0 + 2Aa^{-3}), \quad (2.13) \]

where \( A \) is a constant, \( H_1 \), and \( \mu_1 \) are the field and permeability inside a sphere with radius \( a \), and \( H_0 \), and \( \mu_2 \) are outside the sphere. The factor \( A \) can be eliminated by combining 2.12 and 2.13:

\[ H_1 = H_0 \frac{3\mu_2}{\mu_1 + 2\mu_2} \quad (2.14) \]

The demagnetization field of the sphere is

\[ H_d = H_1 - H_0 \quad (2.15) \]

\[ = -\frac{\mu_1 - \mu_2}{\mu_1 + 2\mu_2} H_0. \quad (2.16) \]

Inserting \( \mu_2 = 1 \) in equation 2.16 gives the magnetization of a sphere in vacuum as

\[ m_1 = -3H_d. \quad (2.17) \]

A sphere in a magnetic medium can be described as a sphere in vacuum with an effectively altered permeability. Inserting 2.16 in 2.17 gives

\[ m_1 = 3 \frac{\mu_1 - \mu_2}{\mu_1 + 2\mu_2} H_0. \quad (2.18) \]

The factor \( 3 \frac{\mu_1 - \mu_2}{\mu_1 + 2\mu_2} \) is the effective permeability and can be written in terms of susceptibility as

\[ \chi_{\text{eff}} = 3 \frac{\chi_1 - \chi_2}{\chi_1 + 2\chi_2 + 3}. \quad (2.19) \]

The effective susceptibility of the magnetic and non-magnetic beads (with the susceptibility \( \chi_m \) and \( \chi_n \)) is

\[ \chi_{m,\text{eff}} = 3 \frac{\chi_m - \chi_{\text{FF}}}{\chi_m + 2\chi_{\text{FF}} + 3}, \quad (2.20) \]

\[ \chi_{n,\text{eff}} = 3 \frac{\chi_{\text{FF}}}{2\chi_{\text{FF}} + 3}, \quad (2.21) \]

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where $\chi_{m,\text{eff}}$ is the susceptibility of the magnetic bead and $\chi_{\text{FF}}$ is the susceptibility of the ferrofluid. If $\chi_1 \ll 1$ and $\chi_{\text{FF}} \ll 1$ the denominator in eq. 2.19 is approximately 3 and the effective susceptibilities of the magnetic and non-magnetic beads can be simplified as

$$\chi_{m,\text{eff}} \approx \chi_m - \chi_{\text{FF}},$$

(2.22)

$$\chi_{n,\text{eff}} \approx -\chi_{\text{FF}}.$$  

(2.23)

The effective susceptibility is the original susceptibility, reduced by the susceptibility of the surrounding medium. The effective susceptibility of the non-magnetic beads is non-zero and, therefore, these beads show magnetic behavior, if an external field is applied. For the non-magnetic beads $\chi_{n,\text{eff}} \leq 0$ and therefore these beads are diamagnetic. For the magnetic ones,

$$\chi_{m,\text{eff}} = \begin{cases} 
< 0, & \text{if } \chi_m < \chi_{\text{FF}} \\
= 0, & \text{if } \chi_m = \chi_{\text{FF}} \\
> 0, & \text{if } \chi_m > \chi_{\text{FF}}
\end{cases}$$

(2.24)

### 2.2.4 Susceptibility dependency

The potential energy between two dipoles is proportional to

$$U \propto m_1 \cdot m_2.$$  

(2.24)

The effective dipole moment of the beads is

$$m_i = V \chi_i \cdot H_{\text{ext}},$$

(2.25)

where $V = \frac{4}{3} \pi a^3$ is the volume of the bead. Inserting the moments into eq. 2.24 gives

$$U \propto V \chi_i \cdot H_{\text{ext}} \cdot V \chi_j \cdot H_{\text{ext}}$$

(2.26)

$$= V^2 \chi_i \chi_j \cdot H_{\text{ext}}^2$$

(2.27)

$$\propto \chi_i \chi_j.$$  

(2.28)

### 2.3 Non-magnetic interactions

In the most simple model colloidal microbeads can be treated as hard spheres. However, the interactions of particles in a colloid can be very complex and a variety of forces needs to be taken into account.

The colloidal stability of particles in liquids is described by the DLVO theory. The colloid is only stable, meaning the particles remain in dispersion, if the repulsive forces between the particles prevent them from sticking to each other. The process of particles sticking to each other and the cluster formation is called flocculation (reversible) or agglomeration (irreversible).
2.3.1 DLVO theory

The DLVO theory (which is named after Derjaguin, Landau, Verwey and Overbeek) describes colloidal stability based on electrostatic and van de Waals forces [38]. Particles with electrical charge on their surface repel each other. The dispersion is overall electrically neutral and the electrical charge on the particle surfaces is balanced by oppositely charged ions in the liquid phase. The distribution of the free ions depends on the electrostatic interaction and the entropy.

The Debye length gives a measure of the length over which the electric field decays. This length depends on the ion density in the solution and is typically less than a few hundreds of nanometer. Therefore, it is small compared to the size of the microbeads.

The cloud of ions around the particle can be divided into different layers. The Stern layer is the first layer directly at the surface. A fraction of the ions is following the particle motion. The boundary of this layer is called the slipping plane. The electric potential at the slipping plane is called zeta-potential. It is an important measure of colloidal systems because it is an indicator for the colloidal stability of charge stabilized particles. It can be measured by applying an electric field and detection of the induced particle motion by dynamic light scattering [39].

The van der Waals or London force is a short ranged attractive force, which is mainly responsible for the agglomeration of colloidal particles. The force results from dipole fluctuations. The potential energy scales with the distance between the molecules as $E \propto r^{-6}$ and, therefore, the force is shorter ranged than permanent dipole or electrostatic interactions. This can be used to prevent van der Waals interaction between particles by keeping them at a distance of a few nanometer from each other. The strength of the force depends on the material and is strong between metals, intermediate between oxides and weak for hydrocarbons [40].

2.3.2 Segmentation

Segmentation of particles depends on density and entropy. Gravitation causes particles to sink or float depending on their effective density, which is the particles density reduced by the density of the dispersion medium. The gravitational force does scale with the effective weight of the particle and, therefore, with the effective density and with the particle size. Entropy increases with the number of particles and causes the particles to distribute homogeneously in the volume. The particle density distribution for an ideal gas is [16]

$$\rho(z) \propto e^{-\frac{z}{\xi_g}},$$  \hspace{1cm} (2.29)

$$\xi_g = \frac{k_B T}{mg},$$  \hspace{1cm} (2.30)
where $z$ is the distance from the bottom of the colloid, $m$ the effective mass of the particle in the suspension, $k_B$ the Boltzmann constant and $T$ the temperature. Segmentation can be induced by flocculation, since clusters are heavier than the individual particles.
3. Methods

Microscopy was used to observe structures of assembled microbeads in a ferrofluid. In this chapter the microscopy set-up, the particles and the analytical methods are described.

3.1 Microscopy setup

Transmission microscopy was used to observe self-assembled structures, the set-up is shown in fig. 3.1.

Figure 3.1. Transmission microscope setup: The sample stage can be moved in all direction by stepper motors. A camera mounted on top of the microscope records images.

The sample, beads dispersed in ferrofluid, was contained between glass slides, which are separated by a polyester ring. The ring was covered with a small amount of oil, which seals the liquid and prevents it from drying. Magnetic coils create a homogeneous magnetic field over the sample area. The coils are mounted at the microscope platform. The in-plane magnetic field can be applied by coils mounted left and right at the microscope platform. For an out-of-plane field a single coil is mounted under the platform. Limitations to create the required field strength are the maximum current that can be applied, so that the coils are overheating and the weight of the coils, as heavy coils may bend the platform. To reduce current and weight the coils are placed as closely as possible to the sample. The custom-build microscope platform
can be moved by stepper motors. The platform and the motor mounts were designed in the open source software FreeCAD [41] and were manufactured with a 3D printer.

3.2 Sample description

The samples were prepared by mixing magnetic and non-magnetic micro beads with ferrofluid, a dispersion of magnetic nanoparticles in water.

3.2.1 Ferrofluid

A suspension of magnetic nanoparticles in a liquid is called ferrofluid (FF). In our experiments a water based ferrofluid with iron oxide nanoparticles, which was purchased from LiquidResearch (UK), has been used. The particles do not agglomerate even with an external field applied, because the thermal energy is higher than the magnetostatic energy between the particles. A picture of the ferrofluid exposed to a magnetic field and a TEM image of the dried particles are shown in fig. 3.2. In a magnetic field, the surface of the FF exhibits a crest pattern due to Rosenberg instability [42]. Due to the high concentration of nanoparticles, the undiluted FF is very opaque. The mean diameter of the Fe$_3$O$_4$ particles is around 10 nm.

![Figure 3.2. Left: Picture of a ferrofluid drop a magnetic field. Right: TEM image of magnetic the nano particles in the dried ferrofluid [43]](image)

The concentration of the magnetic nanoparticles is 9.1% by volume and 34.6% by weight. The magnetic susceptibility can be estimated by the volume fraction of the magnetite in the FF and the bulk susceptibility of magnetite $\chi = 21$ as $\chi_{\text{FF}} = 0.091 \times 21 \approx 1.9$. However, the response of the magnetic nanoparticles is different than that of the magnetic domains in the bulk material. Another method is to measure the magnetic response of the FF by SQUID as shown in fig.3.3.
Figure 3.3. The M-H loop of the ferrofluid measured by SQUID at 10K and 300K (room temperature). The tanh and the Langevin functions are fitted. At 10K the particles can not rotate and show a ferromagnetic response, while at 300K the FF has zero remanence and is superparamagnetic.

At a temperature of 10 K the ferrofluid has a magnetic remanence, because the dispersion medium is frozen and the nanoparticles are unable to rotate. At 300 K, room temperature, the it is liquid and displays a superparamagnetic response. The susceptibility is the slope at H=0 Oe (times $4\pi$ for SI units), which can be calculated by fitting a function that described the expected magnetic behavior, such as the hyperbolic tangent (tanh) function or the Langevin function. For data at 300 K, both functions have been fitted using 20 data-points (of a half-loop) around H=0 Oe. The Langevin function does fit the experimental data better then the tanh. The slope of the Langevin function at H=0 Oe gives $\chi_{FF} \approx 0.53$. The susceptibility as measured by SQUID is around a factor 4 smaller then the estimation from the bulk material.

While microbeads are sinking to the bottom of the containing volume within a few minutes, the nanoparticles in the ferrofluid are in a stable suspension and are not sedimenting even over years. In the case of the ferrofluid the density is very homogenous and was measured with a concentration meter, the DMA 4500 M from Anton Paar, to be 1.361 g/cm$^3$ in the top of the containment and 1.378 g/cm$^3$ in the bottom (in around 10 cm depth). A small fraction of nanoparticles forms visible clusters, which is also reported for other ferrofluids [44]. This clusters are heavier and sediment to the bottom of the batch volume.

## 3.2.2 Microbeads

The microbeads were purchased from Microparticles GmbH (Germany). They are monodisperse spheres with a diameter of 10 μm. Two types of beads are used, both are polystyrene beads, the non-magnetic ones are plain, while the
magnetic beads are coated with a shell of magnetic nanoparticles, as shown in fig. 3.4.

![Figure 3.4](image.png)

**Figure 3.4.** SEM images of magnetic microbeads: The polystyrene core is covered by a shell of magnetic nanoparticles (left image). For some of the magnetic beads the drying process broke of parts of the shells, revealing the core/shell structure (right image).

They are labeled with different dyes and can be distinguish by light microscopy. Different batches were used in the experiments in Paper I and II as shown in fig.3.5.

The beads are dispersed in water, but because of the large size of the beads, sedimentation occurs within a few minutes. The beads that where used in the experiments in Paper I showed excellent stability and did not seem to stick to each other as observed in the microscope. The beads used in Paper II are from a different batch. The magnetic ones appear to be stable, while the non-magnetic ones stick slightly to each other. This can be explained by the lower zeta-potential of the non-magnetic beads, which is -13.9 mV, compared to -47.8 mV for the magnetic ones as measured with the particle analyzer LS500 from Anton Paar. The zeta-potential of the particles can be altered by adding surfactant into the solution or dilution. After the negatively charged solvent SDS was added to the solution of non-magnetic beads, an increased repulsion between pairs of beads was observed by microscopy. With a positively charged solvent added an immediate agglomeration of all beads was observed. This can be explained by reduction of the negative charge of the beads by the added positive charge. Dilution of the colloids can reduce colloidal stability, because the concentration of solvent is reduced and the zeta-potential lowered.
3.3 Image analysis

The beads are detected on the microscope images as circles with the MATLAB® function *imfindcircles* [45]. The beads can be distinguished by type, because one type appears dark and the other one bright in the center. The distinction can be done in two ways. The first method is to search in the image for bright circles. These are circles with gradients pointing outwards, as shown in 3.6 (a).

![Figure 3.6.](image)

*Figure 3.6.* The beads are detected as circles. Types can be distinguished in two ways: Either, (a) for the bright beads a second circle with outwards directed gradients is detected or (b) the brightness of the center pixels is calculated.

To distinguish the types, a threshold has to be defined, so that the dark beads are not wrongly detected as bright ones or bright ones as dark ones. This is done interactively with a graphical user interface (GUI), which is based on the MATLAB® code *Circle Finder* [46], shown in fig. 3.7.
Figure 3.7. FindCirclesGUI: The GUI allows to adjust parameters to detect the beads and observe the result directly. The magnetic beads are marked blue and the non-magnetic ones cyan. Large images are scanned in sections. Beads positions and types can be exported as text files.

Furthermore, parameters are adjusted for both types of beads: detection threshold (more or less circles detected), circle sharpness (more or less blurry circles) and circle radius (minimum and maximum allowed radius). The results can be seen directly by circles drawn over the original image, so that the parameters can be optimized directly. The best threshold for one image is then used for all images on that sample. This method works well, if all images of one sample have the same illumination and are not too blurry (out of focus).

The second method is to calculate for each bead the mean brightness in the center e.g. a rectangular $11 \times 11$ pixels, shown in 3.6 (b). From the center brightness of each bead a histogram is calculated, in which each type appears as a peak. The threshold is then the brightness corresponding to the minimum between the peaks. This method works very well, if there are sufficient beads in the image to calculate the histogram.
The bead positions, bead type and radius are stored for each bead. Images are processed in sections so that for large images the process does not exceed the available memory. Furthermore, the section in which the bead was detected is stored and can be used to speed up further processing of the data.

3.4 Image stitching

The larger maps were made by stitching sets of 220 images together using the open source program Hugin [47]. The single images were taken over the sample in a snake-like pattern with an overlap of around 50%.

In the stitching process characteristic points in the images are detected and correlations are found. Then the images are aligned, so that the points overlap as much as possible. From the single images one large image is fused, as shown in fig. 3.8.

![Figure 3.8](image)

Figure 3.8. From a set of overlapping images a bigger single image is fused. The colored connecting lines show the correlation found. The fused image is chopped to a rectangular shape.

Illuminations and white balances are adjusted, which improves the bead type detection. Furthermore, image quality is improved in the overlapping areas. If one image is out-of-focus, the overlapping areas are taking from the neighboring images, so that they appear sharp.

Additionally, for the large stitched images the sector, in which the bead is located is stored. The sector is a rectangular part of the whole image. This information allows to speed up data processing (e.g. finding neighboring beads) because for each bead only other beads in the neighboring sectors have to be taken into account as candidates for neighboring beads.

3.5 Simulation

Computer simulations can be used, in addition to the experiments, to study the self assembly of the beads. Here, a simple, time evolution is utilized. The simulation complements the experiment, because it allows to cover the whole
parameter space. A difference is that the simulation is closer to an idealized system. In this way, the results might be easier to be interpreted and generalize. A schematic of the steps in the simulation is shown in fig 3.9. In order to minimize the need of introducing experiment specific parameters as well as keeping the simulation run time fast, a few assumptions and simplification have been made:

1. The Brownian motion is neglected.
2. The beads have no momentum and displacement of beads proportional to acting forces.
3. The dipole forces have a cutoff distance.
4. The beads have point-dipole moments.
5. The beads have no induced moments from stray fields.

The simplifications should not essentially alter the outcome of the process, which is justified in the following. (1) Brownian motion is neglected, because the magnetostatic energy is several orders of magnitude higher than the thermal energy. Furthermore, the time at which diffusion occurs is small compared to the time at which the beads self-assemble. (2) A cutoff distance is chosen at 4 diameters. The magnitude of force from a bead in a distance of 4 diameter
is $4^{-4} \approx 0.4\%$ of a force from a bead at 1 diameter distance. However, at very low density beads can be isolated and not move at all. Therefore, every $n$th loop, the cutoff distance is chosen at 6 diameter and the force is up-scaled by a factor of $n$. The error induced by updating the force only every $n$th loop depends on how much the bead positions change in between the steps. The changes are high in the beginning and get lower as the simulations go on. Therefore, at a higher number of iterations $i$, $n$ can be chosen larger, and is set to $n = \text{round}(\sqrt{i})$ for $i > 100$ and $n = 1$ for $n \leq 100$. This is a conservative choice, as the dynamics slow down much quicker than the square root.

(3) The beads are approximated as point dipoles. This is an approximation, as from the SEM images it is known, that the magnetite is rather distributed as a shell around the beads. The error from this difference is expected to be more prominent for beads that are close, because at higher distances the multipole field becomes more similar to the dipole field. (4) Induced moments from stray fields are neglected. This error is difficult to estimate, as it depends on the local susceptibility and the local geometry of the magnetic material. However, the susceptibility $\chi \ll 1$, therefore the external field is larger than the stray field from the surrounding beads. One way to validate the simulation is to compare the simulation results with the experimental results, as shown in 4.2.2.
4. Results and discussion

The self-assembly with in- and out-of-plane was studied and the results are based on the image analysis of microscope images and the extracted bead positions. For an in-plane field, the phase transition from cubic to hexagonal as the FF susceptibility is altered is characterized and the results are published in paper I. For the out-of-plane field, a rich phase diagram was observed, depending on bead density, composition and interaction. The first approach to cover the parameter space was to collect data from a high number of images, as presented in paper II. Complementary to the experiments, computer simulation was used to systematically explore the parameter space as presented in paper III.

4.1 In-plane external magnetic field

The self-assembly for in-plane magnetic fields depends on the magnetic susceptibility of the ferrofluid and square or hexagonal lattices are observed, as shown in fig. 4.1.

Figure 4.1. With increasing FF susceptibility the effective moments of the beads alter. Four cases are distinguished: (a) Only the magnetic beads have an effective moment. (b) The effective moments of the two types of beads are anti-parallel to each other. (c) Only the non-magnetic beads have an effective moment. (d) The effective moments of both types of beads are parallel to each other.

In case with the FF susceptibility equal to zero $FF/\chi_m = 0$, shown in fig. 4.1(a), the magnetic beads form chains or hexagonal lattices, while the non-magnetic beads are randomly distributed. For FF susceptibilities with $0 < FF/\chi_m < 1$, the effective moments of magnetic and non-magnetic beads are anti-parallel
with respect to each other. Square lattices are formed with layers of alternating types of beads, as shown in fig. 4.1(b). If the FF susceptibility is $\frac{\text{FF}}{\chi_m} = 1$, the magnetic beads have effective moments equal to zero. In this case, the non-magnetic beads form chains, while the magnetic beads are randomly distributed, as shown in fig. 4.1(c). For larger FF susceptibilities $\frac{\text{FF}}{\chi_m} > 1$, hexagonal lattices are formed, where the magnetic beads are mostly found at the surface of the clusters. The self-assembled lattices can be seen as stacked layers (or chains) of beads, which are aligned with respect to the external magnetic field. The degree of order with respect to the square and hexagonal lattice is quantified by parameters, which are defined as the radial and angular distribution functions at characteristic distances and angles respectively.

In the case of a periodic structure, the RDF shows sharp peaks at distances that are characteristic for the particular lattice. On the other hand, for amorphous structures this peaks are smeared out and disappear completely for larger distances.

Binary compounds can, additionally, be described by a partial radial distribution function. The partial radial distribution function takes only pairs of particles into account, that are of certain types. In a binary system with types A and B, the possible combinations are [A,A], [A,B], and [B,B]. The partial radial distribution functions describe for each sample the probability to find a magnetic bead and a non-magnetic bead in a distance $R$ from each other, as shown in fig. 4.2.

**Figure 4.2.** Radial distribution functions for four samples. Characteristic length are $\sqrt{2}d$ for square lattice and $\sqrt{3}d$ for hexagonal lattice, where $d$ is the bead diameter.

The RDF is normalized by $4\pi R^2$ and by the average value over all $R$, so that a RDF with a constant value of one corresponds to a random distribution. The
structures can be described by the angular distribution function (ADF) as well. For each bead with two or more neighboring beads, where one is magnetic and one non-magnetic, a (partial) angular distribution function can be defined as the distribution of angles between the lines connecting the beads. Angles of 60° and 120° are characteristic for hexagonal lattice and 90° for square lattice.

The RDF and the ADF at the characteristic length and angles, respectively, parameter that quantify the phase transition between square and hexagonal lattices as shown in fig. 4.3.

![Graph showing RDF and ADF](image)

**Figure 4.3.** The (a) RDF and (b) ADF at evaluated at length and angles, respectively, characteristic for square and hexagonal lattices.
4.2 Out-of-plane external magnetic field

In an out-of-plane field, a variety of structures assemble depending on the bead density, composition and interactions. The results from experiments and simulation are described in the following.

4.2.1 Experimental results

A set of samples was prepared with susceptibilities in the range $\chi_{\text{FF}}/\chi_m = 1/8$ to $3/2$. An average of around 50 images was taken for each sample. The images can be mapped by bead composition and magnetic interaction as shown in fig. 4.4.

![Image of experimental results]

Figure 4.4. A table of experimental images with varying bead ratios $r$ and FF susceptibility. Three phases are highlighted: (left) Flower phase, where one magnetic bead is surrounded by 3-6 non-magnetic beads, (center) mixed cubic lattice and branching chains, (right) isolated beads

However, the bead density varies between the images and can be inhomogeneous within an image. The ratios are not precise, but the image with the closest ratio to the nominal one is chosen. From the table of images, three images are highlighted. First, with a low FF susceptibility $\chi_{\text{FF}}/\chi_m = 1/8$ and a bead ratio of $r = n_m/n_n = 1 : 5$ the formation of 'flowers', one type of bead surrounded by a ring of the opposite type, is observed. Second, at $\chi_{\text{FF}}/\chi_m = 1/2$
and a bead ratio of $r = 1 : 1$ chains and square lattices are assembled. For this susceptibility, the interactions are close to symmetric, because the magnitudes of moments of the magnetic and non-magnetic beads are close to equal (but with opposite sign). In the third case at $FF/\chi_m = 3/2$ all beads are isolated, because the effective moments of both types of beads are parallel to each other and, therefore, all interactions are repulsive. It is observed, that the distance between two magnetic beads that are next to each other is smaller than for two non-magnetic beads. The table of images shows a rich phase diagram that depend on bead density, composition and interaction. Because of the many combinations of parameters, a large set of images is required to cover the entire parameter space.

An alternative to analyze many single images is to use large stitched images. For the large images, artifacts from image borders are reduced and longer range correlation between the beads can be found. An example with $\chi_{FF}/\chi_m = 1/4$ is shown in fig. 4.5.

![Stitched Image](image.png)

*Figure 4.5. A stitched image with characteristic structures. The number of detected beads is around 80,000 in an area of around 10 mm$^2$. The bar is 1 mm.*
In this large images, the parameters such as density are not homogeneous over the sample and it is not meaningful to calculate the average. Instead, the parameters are calculated locally and for each bead the number of magnetic and non-magnetic beads within a radius of 5 bead diameter is counted. The circle radius is set to 5 bead diameters, because the RDF is one on a longer distance, indicating no longer range correlation. The density is the total number of counts for both types normalized by the density of close-packing, so that zero describes a completely isolated bead and one refers to the highest possible value. The bead composition is the fraction of magnetic beads and the fraction is zero if the bead is surrounded by only non-magnetic beads and one for only magnetic ones. For the sample with FF susceptibility $\chi_{FF}/\chi_m = 1/4$, the local cluster size, the density and the composition are shown in fig. 4.6.

Figure 4.6. The cluster sizes, density and composition for the sample with $\chi_{FF}/\chi_m = 1/4$: (a) Each cluster of connected beads has one (random) color. (b) The density varies with an approximate gradient from the top left corner to the bottom right corner. (c) The bead composition. The colorbar in (c) applies also to (b). Three characteristic areas are highlighted, as shown at the right side of each colormap.
Three different characteristic areas are highlighted. First, for low density and a symmetric composition $r \approx 0.5$ short chains are assembled. Secondly, at above medium density and symmetric composition, large clusters form. Third, at high density and high $r$, many beads are isolated and relatively small clusters are assembled. The self assembly depends on the bead density. At high density, jamming occurs and leads to frustrated structures. At low density the beads can be isolated and do not interact with each other. Cluster sizes do generally grow with the density. For each bead the size of the cluster in which it is located is calculated. In a first step, all direct neighbors are defined by a distance between their centers that is smaller than a threshold, which is the mean bead diameter times a factor of 1.05. While this factor would be 1 for ideal hard spheres, it is slightly larger in reality due to electrostatic repulsion and thermal motion. Furthermore, the diameter can vary a few percent for each bead. The clusters are detected by starting with one bead and iteratively adding neighboring beads to the cluster. The cluster size is not strictly a local variable because the cluster can extend over a large area. Interesting are cases with large clusters with lower densities. The average cluster size depends on the density and composition as shown in paper II.

4.2.2 Simulation results

While it is difficult to cover the whole parameter space experimentally, the parameters can be chosen freely in a simulation, so that phase mapping is only limited by computation power and simulation time. A simple simulation that only uses a few parameter has been used to map the parameter space, bead density, composition and interaction. A total of 600 combinations were simulated with 15,000 time steps, where the simulation runs over 3 weeks. To be meaningful, the simulation results have to reflect the experiment. Therefore, the results from experiments and simulation are compared for bead ratios $r = 1:1$ and $r = 1:6$ and different FF susceptibilities. The same densities in the experimental data vary from image to image and for the simulation the same values are chosen for comparison. The bead positions are extracted from the experimental data and the clusters have been detected for both, experiment and simulation as shown in fig. 4.7.

In the simulation the beads are distributed more homogeneously. Noticeably, for a bead ratio $r = 1:6$ the beads are less connected to each other than for a bead ratio $r = 1:1$ in the experiments as well as in the simulation. The percolation is the extent to which the beads are connected. The degree of percolation can be defined as the mean cluster size divided by the number of beads, so that a value close to zero corresponds to isolated beads and a value of one to fully connected beads. The percolation of beads is related to their coordination number.
Figure 4.7. Clusters for experimental and simulation data. A random color is assigned to each cluster of connected beads. The numbers of beads extracted from the microscope images are used as parameters for the simulation.

The experimental results can be compared to simulation by subdividing it into the same parameter space. For the mean coordination number and degree of percolation, the comparison is shown in fig. 4.8. However, the experimental data only covers around 1/5 of the parameter space, even though the total number of data sets is similar (500 images, 600 simulations). The experimental data seems to be more noisy, when comparing the correlation between neighboring data points. A reason could be the density fluctuations. Most noticeable, the coordination number and percolation increase with the density. The percolation is for all densities small at compositions \( r \geq 3 \).
Figure 4.8. Comparison between experimental and simulation data, where the color maps show (a) the mean coordination number and (b) the percolation, depending on bead ratio and interaction for different densities (the axis labels are shown below the color maps). The experimental data covers the parameters space (600 parameter combinations) only sparsely (missing data is colored in black).
4.3 Lattices, chains and flowers

Structures are assembled with different dimensions. The dimension can be natural number:

- 0D isolated beads and flowers
- 1D chains of beads
- 2D planar structures

For an out-of-plane field and FF susceptibility $\chi_{FF}/\chi_m > 1$ the beads are isolated as shown in fig. 4.9. All beads repulse each other and the interaction strength depends on the product of effective moments. This is strongest for a pair of non-magnetic beads and weakest for a pair of magnetic beads, and a medium strength for a mixed pair. The average pair distance of close beads varies with the interaction strength, with a stronger repulsive force leading to larger distances. It can be noted that the beads demix to some extend, so that the magnetic ones are more likely to appear in groups. Demixing is also observed in the case of in-plane fields for beads with parallel moments but different strength of moments, where the magnetic beads are found at the outside of the hexagonal clusters.

Flowers are formed, when the effective moment of one type of bead is much larger then the other. This is the case at FF susceptibilities $\chi_{FF}/\chi_m \gtrless 0$ ($m_M \gg m_N$) or $\chi_{FF}/\chi_m \lesssim 1$ ($m_N \gg m_M$). In this case one bead (e.g. a magnetic one) with a high moment can be surrounded by 3-6 beads (e.g. non-magnetic ones) with low moments, because the attractive force, in this case, $F \propto m_M \times m_N$ of the surrounding beads to the center bead is bigger then the repulsive force between them $F \propto m_N \times m_N$. The number of possible surrounding beads is determined by the interaction potential and as their number increases

![Figure 4.9. The moments of both types of beads are parallel to each other, so that all beads repulse each other. The distance between two magnetic ones is smallest, followed by a combination of one magnetic and one non-magnetic bead and is largest for two non-magnetic beads. The simulation results are in good qualitative agreement with the experimental results.](image)
the repulsive force from the other surrounding beads increases. Therefore, the maximum number of surrounding beads increases with the ratio of the effective moment of the center bead to that of the surrounding beads.

Chain formation can occur both for in-plane and out-of-plane magnetic fields, as shown in fig. 4.10. In the case of in-plane fields chains are assembled by one type of beads and aligned along the external field lines. In the case of out-of-plane fields, the chains are randomly oriented and less straight, since the only force preventing curvature is the repulsive force between next-nearest neighbors. In both cases, chain growth is driven by stronger stray fields at the ends of the chains, attracting free beads. Examples for chains for both cases are shown in fig. 4.10.

![Figure 4.10. Chains for in-plane (a) and out-of-plane (b) magnetic fields.](image)

The formation of lattices is observed for in-plane and out-of-plane fields, as shown in fig. 4.11. Lattices are assembled if the bead composition matches the interactions. Additionally, the density of beads has to be high enough.

Square lattices are observed for both in-plane and out-of-plane external fields, when the FF susceptibility is $\chi_{\text{FF}}/\chi_m \approx 0.5$ and the interaction is symmetric. However, they differ in the distribution of magnetic and non-magnetic beads. For in-plane fields, the lattice consists of alternating layers of magnetic and non-magnetic beads, while for the case of out-of-plane fields, each bead of one type is surrounded by four beads of the opposite type.

The hexagonal lattice occurs in both cases, but at different susceptibilities. For the in-plane case, the FF susceptibility is $\chi_{\text{FF}}/\chi_m > 1$ with the moments of both types of beads parallel to each other but with different magnitudes of the effective moments. Since the effective moments of the non-magnetic beads higher, the interaction potential between two non-magnetic beads is stronger and the magnetic beads are pushed towards the surfaces of the clusters. This demixing is similar to the demixing of water and oil, where the water-water interaction potential is much higher the oil-water potential.
In the case of the out-of-plane field, the hexagonal lattice occurs at FF susceptibilities, where one type of bead has a high moment and the other one a low moment. Each type of beads forms a sub-lattice, as shown in 4.12.

The different types of hexagonal lattices can be seen as super-structures composed of the 6-fold flowers. In the honeycomb lattice a pair of flowers shares two 'leaves' and each leaf is shared by three flowers, so that the bead ratio is \( r = 1/3 \cdot \frac{1}{6} = 1 : 2 \). In the kagome lattice, a pair of flowers share one leaf and each leaf is shared by two flowers, leading to a bead ratio of \( r = 1/2 \cdot \frac{1}{6} = 1 : 3 \). Additionally to the different bead ratios, the bead interactions are different, which is related to the distances between the center beads. For the honeycomb two center beads are in a distance of \( d_H = \sqrt{3}d \approx 1.7d \), while for the kagome the distance is \( d_K = 2d \), where \( d \) is the bead diameter. A higher distance between the center beads is related the repulsive force between them, which is \( F_{M-M} = m_M^2 \), if the center beads are magnetic ones with effective moment \( m_M \). Therefore, the sub-lattice depends on both, the FF susceptibility \( \chi_{FF}/\chi_m \) and bead composition \( r \).

The square phases for the in- and out-of-plane phase can be interpreted as projections of a cubic lattice in 3D space as shown in fig. 4.13.

However, the assembly process in 3D would be different, because of the higher degree of freedom in the motion of beads. Furthermore, for the case \( \chi_{FF}/\chi_m > 1 \), the out-of-plane assembly is very different from the 3D projec-
Figure 4.12. The hexagonal out-of-plane lattice can have different sub-lattices like hexagonal or kagome. These can be seen as super-structures, build by the 6-fold flowers. The distances between the center beads of the flowers varies between the sub-lattices.

Figure 4.13. The in-plane and out-of-plane square lattices shown as projections of a cubic lattice in 3D space.

tion, because the beads do not assemble in a plane and, therefore, the dipole interaction are different.

4.4 Stable States, Meta-stable states, and dynamically arrested states

In both cases, out-of-plane and in-plane, lattices and branching chains are observed. The lattice structure is in general the lowest energy state. However, the growth process can favor the chain formation. One example is for assembly with out-of-plane field and beads with magnetic moments 1 and −1 for the magnetic and the non-magnetic type, respectively. In a first step, one
magnetic and one non-magnetic bead can form a pair with zero total magnetic
dipole moment, but a quadropole moment. The next bead that can be joined to
the pair will then be attached to the end of the 2-chain, so that a 3-chain with
alternating bead type is formed. In that way a n-chain can grow.

4.5 Fractal dimension

Non-close packed structures can be described by a fractal dimension, which
can be defined [48] for clusters as

\[ d = \frac{\ln(N)}{\ln(R)}, \]  

(4.1)

where \( N \) is the number of beads and \( R \) is the radius of gyration of the cluster.
The radius of gyration is defined as

\[ R = \sqrt{\frac{1}{N} \sum (r_i - \bar{r})^2}, \]  

(4.2)

where \( N \) is the number of beads, \( r_i \) is the position of each bead in the cluster
and \( \bar{r} \) is the mean value of all bead positions.
The fractal dimension is calculated by a linear regression of all clusters, and
the dimension is \( d=1.63-1.91 \) for the different samples. A correlation between
the fractal dimension and the susceptibility \( \chi_{\text{FF}} \) cannot be derived from the
data, because the density and composition vary between the samples. Overall,
the assembled structures are more similar to 2D clusters than to 1D chains. A
study on the fractal dimension of a colloid similar to the here presented and
with applied in-plane-field can be found in literature and a fractal dimension
between 0.94 and 1.54 was reported [48].
Self-assembly of building blocks with tunable magnetic interactions and the analysis of the assembled structures is presented. The results are based on experiments and computer simulation for in- and out-of-plane applied magnetic fields. With an applied in-plane magnetic field self-assembly of square and hexagonal lattice is observed and the phase transition with the varying FF susceptibility is described in paper I. The out-of-plane case is studied by experiments and simulation. The challenge is the variety of phases as well as the high number of parameters. For the experiments, the microscope was automated with 3D printed parts and stepper motors to allow the collection of a large amount of data. Six samples with different FF susceptibilities were prepared and of each 400 images were taken, covering an area of $3 \times 3\text{mm}^2$ with 50,000 to 100,000 beads. In this way most of the parameter space is covered and the results are published in paper II. In order to expand to the entire parameter space computer simulation is employed and validated by comparison to the experimental results. In the simulation 600 combinations of bead density, ratio and interactions were systematically chosen.

The assembly of different lattices and disordered structures is observed depending on the direction of the external field and the sample parameters.

The results are based on the analysis of the final structures. Further studies could explore the dynamics during the self-assembly by evaluating videos from the experiment and intermediate states from the simulation. The dynamics are especially important, because the system does not reach the configuration with the global energy minimum, which could be calculated from the dipole interactions. Instead, the occupation of the meta-stable states is process dependent.

For all studies, beads of micrometer sizes were used. In this case, the free energy is equal to the inner energy and thermal motion does not play a role. One route to expand the studies is to gradually reduce the Boltzmann factor. Different ratios of thermal energy to particle interaction could be realized by the use of smaller beads with varying sizes and the change of magnetic field strength. In this way, the boundary between ordered and disordered structures could be further investigated.

Additionally to having a smaller Boltzmann factor, sub-micron beads can assemble structures with a periodicity on the wavelength of light, which can create structural coloration, as shown in fig. 5.1.

The color depends on the distance between the beads, which can be tuned by changing the strength of the applied magnetic field [9, 49, 50]. One interesting application would be in stereolithographic 3D printing. It has been
Figure 5.1. A shift in color can be observed, when 270 nm particles are exposed to a magnetic field, because chains are formed along the field lines with a periodicity on the length scale of visible light. In the top-left corner a dense packed photonic crystal has grown by sedimentation. The colors of the sample are viewing angle dependent.

reported that magnetic particles in a resin can be aligned by an applied external magnetic field [51, 52, 53]. The applied field could be varied during the 3D printing process to control the structure of the particles locally within the printed object to create different colors.
Selbstassemblierung beschreibt wie sich Bausteine auf den unterschiedlichsten Längenskalen zu neuen Strukturen zusammenfügen, angetrieben durch ihre Wechselwirkung. Vielleicht wird sich eine der spannendsten Fragen der Wissenschaft - der Ursprung des Lebens - durch molekulare Selbstassemblierung erklären lassen.


7. Svensk sammanfattning

Självordning beskriver hur byggstenar, drivna av sina interaktioner, formar olika strukturer på alla längdskalor. Kanske kommer en av de mest spännande frågorna inom vetenskapen - livets ursprung - förklaras av molekylernas självordning.


hittade väldigt många olika strukturer, som isolerade kolor, kedjestrukturer och världnade kristaller beroende på dessa parametrar. För att systematiskt undersöka parametrarna kompletterades experimenten med datorsimuleringar. Verktygen som utvecklades i denna avhandling möjliggör förståelsen för hur själforningen resulterar i olika strukturar.
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