Master thesis, 30 hp
Division for Materials Physics
Department of Physics and Astronomy
Uppsala University
Popular summery

Magnetism is a well known phenomenon since magnetic effects and magnets have various applications present in everyday life. Some examples are orientation by probing the earth magnetic field, fixations such as fridge magnets or magnetic data storage in hard discs. Common to most applications is that solid materials are used as magnets and knowledge of liquid magnetic materials is much less widespread. The reason for this is twofold. First, when thinking about magnetism, most people have materials in mind which show a ferromagnetic behaviour. Secondly, all materials showing a ferromagnetic behaviour at room temperatures are solids. The reason behind the second point is that for temperatures above the melting point generally the thermal energy is so high that the magnetic fluctuations are too large to show ferromagnetic properties. Some liquids are known to show paramagnetic behaviour, such as liquid oxygen, but their magnetic response, called susceptibility, is orders of magnitude lower than the one of ferromagnets. An alternative route to create a liquid with strong magnetic response is the dispersion of small ferromagnetic particles in a solvent. On a small length scale these particles still show ferromagnetic properties and are solid materials. However, on larger length scales, such as micrometer, the character of the individual particles is not directly visible anymore and macroscopically such a material will behave like a paramagnetic liquid, but with a much higher magnetic susceptibility. This kind of magnetism that results from the alignment of microscopic ferromagnets in an external magnetic field is called super-paramagnetism. Mixtures of small particles and liquids are called colloidal suspensions and in the case of magnetic nanoparticles they are often called more specifically ferrofluids. In this thesis a new route of addressing self-organisation in such materials is presented. The basic idea behind it is that a magnetic liquid containing nanometer sized magnetite particles is used as solvent for micrometer sized
ferromagnetic and diamagnetic particles. Following along this route the effective magnetic behaviour of the particles is altered since they replace ferrofluid in a certain volume. This effect can be seen analogue to the Archimedes principle, which is known by everyone and experienced in every-days life since it allows objects with a mass density smaller than water to float.

The approach described above makes it possible to tune the magnetic properties of the micrometer sized particles by changing the concentration of nanometer sized particles in the solvent and thus the effective magnetic behaviour of the large particles. Due to the magnetic interaction, the larger particles arrange themselves in lattices. By changing the ferrofluid concentration the magnetic susceptibility of the solvent is changed and the effective susceptibility of the larger particles is altered. Therefore the interaction between them is tuneable and different structural arrangements can be created. Here we have studied the phase transition from cubic to hexagonal ordering while continuously increasing the magnetic susceptibility of the solvent. The positions of the particles were visualised by particle specific dyes and the use of an optical microscope. The individual particle positions were evaluated automatically and a model to quantitatively explain the results is presented.
Abstract

In this thesis the assembly of magnetic and non-magnetic beads in a water based ferrofluid (FF) in an external homogeneous magnetic field is analysed. The beads show a magnetic behaviour that is described by effective magnetic moments. This is analogue to the Archimedes principle for weights in gravitation.

In a magnetic field the beads arrange in a lattice. Phase transitions with variation of the FF concentration from hexagonal to random and from random to cubic order are quantified and theoretically explained.

A microscope has been used to observe the behaviour of the beads in a magnetic field in situ. Matlab was used to distinguish the beads and analyse the structure based on the distribution of distances between them.
Sammanfattning

In det här arbetet analyseras formationen av magnetiska och icke-magnetiska kulor i en vattenbaserad ferrofluid i ett externt homogent magnetiskt fält. Kulorna visar ett magnetiskt uppförande som kan beskrivas med effektiva magnetiska moment. Detta är analogt med Archimedes princip för tyngd i gravitationen.

I ett magnetiskt fält arrangerar kulorna sig i ett gitter. Fasövergångar varierar beroende av koncentrationen av FF från hexagonal till slumpartad och från slumpartad till kubisk ordning, vilket i detta arbete kvantifieras och förklaras teoretiskt.

Med hjälp av ett mikroskåp har kulornas uppförande i ett magnetiskt fält observerats in situ. Matlab har använts för att detektera kulorna och analysera strukturen baserat på fördelning av distansen mellan kulorna.
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1

Introduction

In this thesis the self-organisation of particles in a ferrofluid is analysed. A ferrofluid (FF) is a liquid with dispersed magnetic nanoparticles. The particles are so small that the Brownian motion prevents them from agglomerating, even in a strong magnetic field.

Figure 1.1 presents some examples for applications and fields of research. Image 1.1 a) shows the use as data storage. A Ferrofluid with monodisperse FePt nanoparticles is slowly dried so that the particles arrange close-packed on a SiO surface. The material FePt is ferromagnetic even for nanoparticles. Each particle can store one bit by its magnetic orientation.

In 1.1 b) the self organisation of microparticles, which are dispersed in FF, to the formation of rings is shown. The rings are produced by using a mixture of three different kinds of beads: Non-magnetic beads with a diameter of $1 \mu m$ (red) form rings around paramagnetic beads with a diameter of $2.7 \mu m$ (dark). The paramagnetic beads themself form rings around a non-magnetic bead with a diameter of $9.9 \mu m$ (green).

Figure 1.1 c) shows the self organisation of particles dispersed in ferrofluid to photonic crystals. The diameter of the used particles is $185 nm$. When particles arrange themselfs into colloidal crystals with lattice constants with half of the wavelength of visible light, photonic crystals are formed. These crystals reflect incident light.

The picture 1.1 d) shows the use of ferrofluid in nail polish. In the lid of the product is a permanent solid magnet with a special pattern. Before the nail polish is dried on the nail, the solid magnet can be held over the nail to reproduce the pattern on the nail polish as shown in the picture.

Another application is with sealing, where the attraction of FF in magnetic
fields is used, to hold the FF in a certain position. The FF acts as a physical barrier. Since the FF is liquid this seal can be used to connect rotating parts, e.g. a rotation shaft and the respective opening of a vessel[1].

In a similar way it is used in loudspeakers. A magnet holds the FF in contact to the membrane to dampen unwanted vibrations.

An interesting field of research is the application of FF in medicine. If the nanoparticles have a functionalized surface that attaches to tumour cells, it could be used as a marker. Strong oscillating magnetic fields can be used to heat the particles and destroy the cells [2]. Another approach is to attach a drug to the FF particles to concentrate the drug in the tumour [3].

These applications were pioneered by important research results, e.g. self-

Figure 1.1: Four examples for the use of ferrofluid are shown: a) Data storage [4] b) Self-Assembly of colloidal rings [5] c) Photonic crystal [6] d) Nail polish [7].

assembly of non-magnetic particles in FF was found and described already in the early 80’s [8]. In early papers in this field only a few different structures were observed [8] [9]. More recent research analysing self assembly in mixtures of magnetic and non-magnetic particles in FF shows a huge variety
of possible structures and a very complex phase diagram[10].
The article mentioned above[10] focuses self-assembly in a 2D system with out-of-plane magnetic fields, and also chain structures in in-plane-fields were observed.
The goal of this thesis was to analyses the structures of alternating chains of magnetic and non-magnetic beads. One question was which structures these chains form and if phase transitions appear.
The system analysed in this thesis is a suspension of magnetic and non-magnetic beads in a water based ferrofluid in a two-dimensional confinement.

Light microscopy has been used to observe the system in situ. A pair of Helmholtz coils produces a homogeneous magnetic field at the focus point of the microscope. To distinguish the different beads the magnetic beads have been labelled with a dye that absorbs blue light. Blue light from a LED is used to illuminate the sample so that the magnetic beads appear dark and the non-magnetic beads appear bright.
The images are analysed by Matlab, which detects both kinds of beads as bright and dark circles and saves their positions. The distribution of distances between the beads can be calculated. For each sample a set of images is analysed and the mean distribution and standard deviation are calculated. Peaks at characteristic distances for a cubic or hexagonal structure are identified and quantified by an error weighted gauss fit.
Samples have been made and analysed for a range of different FF concentrations. By the change of amplitudes of both peaks at different ferrofluid concentrations phase transitions are characterised.
2

Theoretical Background

The arrangement of the particles in the ferrofluid can be understood as the minimisation of magnetostatic energy. The basic concept to describe the energy is the magnetic dipole interaction. The magnetic dipoles of the particles can be explained by their magnetic susceptibility.

2.1 Magnetic Dipoles

In a uniform magnetic field with the flux density $B_{\text{ext}}$ a torque $L$ acts on a magnetic dipole with the magnetic dipole moment $m$ as [11]

$$L = -mB_{\text{ext}} \cdot \sin(\theta)$$ (2.1)

where $\theta$ is the angle between the magnetic field and the direction of magnetisation of the dipole.

Integration over $\theta$ gives the potential energy

$$U = -mB_{\text{ext}} \cdot \cos(\theta)$$ (2.2)

If the magnetic field with flux density $\vec{B}$ is inhomogeneous a force $\vec{F}$ acts on the dipole

$$\vec{F} = m \nabla \vec{B}$$ (2.3)

where $\nabla \vec{B}$ is the gradient of the magnetic flux density.

The magnetic dipole itself produces a magnetic field that can be described
The magnetic dipole $m$ has the angle $\theta$ to the homogeneous field $B_{\text{ext}}$.

in a position relative to the dipole in polar coordinates as

\[
B_r = \frac{\mu_0}{4\pi} m_1 \cdot \frac{2\cos(\theta_1)}{r^3}
\]

\[
B_\theta = \frac{\mu_0}{4\pi} m_1 \cdot \frac{\sin(\theta_1)}{r^3}
\]

(2.4)

where $\mu_0$ is the vacuum permeability.

The angular potential energy between two dipoles $m_1$ and $m_2$ with the distance $r$ to each other can be derived by the formula for the angular potential energy (equation 2.2). The angles $\theta_1$ and $\theta_2$ are each dipoles angular displacement from the straight line through both dipoles (see figure 2.3).

The radial field component of the first dipole at the position of the second dipole is the field strength in the direction of the line through both dipoles. Therefore it is multiplied by $\cos(\theta_2)$ (see eq. 2.2). The tangential component
$B_\theta$ is rotated by $90^\circ$ and has to be multiplied with $\sin(\theta_2)$ respectively. The energy $U$ is the sum of both components

\[
U = -m B_{\text{ext}} \cdot \cos(\theta_2) \quad \quad \quad (2.5)
\]
\[
= -m (B_r \cos(\theta_2) + B_\theta \cos(\theta_2 + \pi/2)) \quad \quad \quad (2.6)
\]
\[
= -m (B_r \cos(\theta_2) - B_\theta \sin(\theta_2)) \quad \quad \quad (2.7)
\]

Inserting the field from equation 2.4 gives

\[
U = -\frac{\mu_0}{4\pi} \cdot \frac{m_1 m_2}{r^3} \cdot (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2) \quad \quad \quad (2.8)
\]

\[
\text{Figure 2.3: } \text{Two magnetic dipoles and the respective angles to the line that goes through both dipoles are shown.}
\]

For dipoles with equal moments $m = m_1 = m_2$ and with the same angle $\theta = \theta_1 = \theta_2$ this simplifies to

\[
U = -\frac{\mu_0}{4\pi} \cdot \frac{3m^2}{r^3} \cdot (\cos^2 \theta - \frac{1}{3}) \quad \quad \quad (2.9)
\]

which is minimal for $\theta = 0$ as

\[
U = -\frac{\mu_0}{2\pi} \cdot \frac{m^2}{r^3} \quad \quad \quad (2.10)
\]

This means, that free magnetic dipoles minimize the angular potential energy by parallelizing.
2.2 Magnetic Susceptibility

The magnetic flux density $\vec{B}$ in a material is defined as

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$  \hspace{1cm} (2.11)

where $\vec{M}$ is the magnetisation of the material. If the magnetisation is a linear function of the external magnetic field, $M$ is given by

$$\vec{M} = \chi \vec{H}$$  \hspace{1cm} (2.12)

where the factor $\chi$ is called magnetic susceptibility.

Materials with a susceptibility $\chi > 0$ are called paramagnetic and materials with $\chi < 0$ are called diamagnetic.

The magnetic flux density of paramagnetic materials in a homogeneous magnetic field is higher than the flux outside of the material (see figure 2.4) and is lower in the case of a diamagnetic material.

![Figure 2.4: Magnetic flux density in and outside of a paramagnetic cylinder in a homogeneous magnetic field: The field inside a paramagnetic material is increased by the magnetisation of the material.](image)

2.3 Effective Susceptibility

The effective magnetic susceptibility is that of the bead minus the one of the displaced ferrofluid within the volume of the bead. This leads to a effective susceptibility of the beads in the ferrofluid that differ from those, which they
would have in water. The principle is analogue to the Archimedes principle. The Archimedes principle states that the effective weight of an object in a liquid is the objects weight minus the weight of the displaced liquid. In the case of the effective dipole moment in a ferrofluid the corresponding force is not the gravitational but the magnetic force.

In a magnetic field the effective susceptibility leads to corresponding effective magnetic moments.

The effective dipole moment of these particles is [13]

\[
\vec{m}_i = 4\pi a^3 \frac{\chi_i - \chi_f}{\chi_i + 2\chi_f + 3} \cdot \vec{H}_{\text{ext}}
\]  

(2.13)

where \( a \) is the particle radius, \( \chi_i \) is the particle susceptibility, \( \chi_f \) is the susceptibility of the ferrofluid and \( H_{\text{ext}} \) is the external magnetic field.

**Figure 2.5:** Effective susceptibilities of magnetic and non-magnetic beads in ferrofluid are shown, the real system is in the top and effective system in the bottom. Four different cases exist: a) \( \chi_f = 0 \) b) \( 0 < \chi_f < \chi_m \) c) \( \chi_f = \chi_m \) d) \( \chi_f > \chi_m \).

The positioning of each particle can be best understood by its magneto-
static potential energy, which is given as [13]:

$$U_i(\vec{r}) = -2\pi a^3 \mu_0 \frac{\chi_i - \chi_f}{\chi_i + 2\chi_f + 3} |\vec{H}_{\text{ext}}(\vec{r})|^2$$ (2.14)

For $\chi_i > \chi_f$ the particles behave paramagnetically, and the potential energy is always negative and minimal at the maximum magnetic field. For $\chi_i < \chi_f$ the particles show a diamagnetic behaviour and the potential energy is lowest in small magnetic fields. The non-magnetic particles will always behave diamagnetically in a ferrofluid with an effective dipole moment

$$m_i = 4\pi a^3 \frac{-\chi_f}{2\chi_f + 3} \cdot H_{\text{ext}}$$ (2.15)

but if the FF is diluted and the magnetic susceptibility of the FF is low, than the susceptibility of these particles will also be low. At the limit of FF concentration/susceptibility goes to zero the particles will behave non-magnetically again.

The magnetic particles can have different effective dipole moments in the ferrofluid. In highly concentrated FF with $\chi_i < \chi_f$ they show diamagnetic behaviour. For $\chi_i = \chi_f$ they can appear non-magnetic and for $\chi_i > \chi_f$ they remain para-magnetic (see figure 2.5).

The potential energy and the force between two beads is proportional to the magnetisation of each bead and therefore also to each effective susceptibility:

$$F \propto \left| -\frac{\chi_f}{2\chi_f + 3} \cdot \frac{\chi_m - \chi_f}{\chi_i + 2\chi_f + 3} \right|$$ (2.16)

For small values $\chi_f << 3$ and $\chi_i << 3$ both susceptibilities are almost linear, since the denominator is constant ($\chi_m + 2\chi_f + 3 \approx 3$). The resulting force can then be written as

$$F \propto |\chi_m \chi_f - \chi_f^2|$$ (2.17)

From this it follows that the force between magnetic and non-magnetic beads is zero for $\chi_m = \chi_f$. This case is shown in figure 2.5 c). The derivative of the force as a function of the FF susceptibility is

$$\frac{\partial F}{\partial \chi_f} \propto |\chi_m - 2\chi_f| = 0$$ (2.18)
This gives a maximum in the dipole force between the two types of particles at

\[ \Rightarrow \chi_f = \frac{1}{2} \chi_m \]  

(2.19)

### 2.4 Lattice

Two-dimensional cubic and hexagonal lattices can be identified by characteristic distances between the beads. These can be derived with the Pythagorean theorem for the cubic lattice as

\[ d_{\text{cub}} = d_0 \cdot \sqrt{a^2 + b^2} \]  

(2.20)

and for the hexagonal lattice as

\[ d_{\text{hex}} = d_0 \cdot \sqrt{\left(\frac{a + b \mod 2}{2}\right)^2 + \frac{3}{4} b^2} \]  

(2.21)

where \( a, b \in \mathcal{N} \) and \( d_0 \) is the distance between direct neighbours, which is two times the bead radius. In the hexagonal lattice each second row is shifted, which leads to the modulo-2 term.

The first characteristic distances for both lattices are drawn in figure 2.6. In a perfect cubic lattice a bead has 4 direct neighbours and 4 neighbours at the distance \( d = d_0 \sqrt{2} \), while in the hexagonal lattice a bead has 6 direct neighbours and 12 neighbours at the distance \( d = d_0 \sqrt{3} \).

In a random distribution the number of neighbours in a certain distance \( d \pm \Delta d \) is proportional to \( d^2 \), since the area in which beads are counted is a ring with the diameter \( d \).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{lattice_diagram}
\caption{Cubic and hexagonal lattices have different characteristic distances, the smallest ones for each case are shown.}
\end{figure}
3

Methods

3.1 Microscopy

Fluorescent materials absorb light and emit it with a longer wavelength. This is used in Fluorescence Microscopy, a method where fluorescent areas of a sample are made visible with the help of filters (see figure 3.1). The filters are chosen so that the transmitted light from the first filter is completely absorbed by the second filter. The first filter is positioned before the sample. The wavelength of the transmitted light from this first filter should be close to the absorption maximum of the fluorescent material. The second filter stops the direct light but is transparent for the fluorescent light.

3.2 Sample Cell

A liquid cell and a pair of Helmholtz coils are held by an aluminium construction on a rigid steel arm (as shown in figure 3.2). The construction consists of a four-sided ring and an aluminium bottom plate. The ring holds the coils and is, together with the liquid cell, placed upon the bottom plate. The bottom plate is 3 mm thick, the thickness is limited by the microscope lift, and connected to the rigid arm at one side.

The colloid is enclosed in the liquid cell (shown in figure 3.3). The cell consists of a thick bottom glass plate and a thin top plate. Both glass plates are separated by a Mylar spacer. The spacers are in the form of rings with 6, 12 and 25 $\mu$m thickness. The colloid is framed by the plates in the vertical
direction and by the spacers in the horizontal direction. The glasses with the spacer are held by an aluminium cell with rubber layers between the glass and the aluminium. Four screws, one at each corner, allow exerting force on the glasses in a controlled way.

The coils are driven by a power supply. The power supply can produce a voltage up to 60 V and a current up to 18 A. The output voltage and the maximal current can be controlled by a little input voltage between 0 and 5 volt. This voltage is produced by an analogue output unit "NI USB 6009" from national instruments. It can be controlled by the computer via a LabView program. Both values can be regulated manually or in a predefined way. Since the resistance of the coils can change, the power supply controls the current instead of the voltage to produce a well-defined magnetic field.

A LabView program has been written (as mentioned above) to control the current in the coils. The program is shown in a block diagram with the different functions in figure A.1 (in the Appendix). Since the controlled instrument has no hardware timer, the time is controlled by the speed at which the main loop is executed. The voltage can be set manually but since the supply should be limited by the current during the cycle, it has no influence as long as it is set high enough.

The current is set as a square function shown in the Appendix figure A.2. One cycle takes 3 seconds. It is split up, where 2.55 s is high current and 0.45 s...
The transition between high current and the current is slightly smoothed to reduce possible artefacts and impedance effects from the inductance of the coils.

The Helmholtz coils provide the external in-plane magnetic field. The coils are connected in series. The resistance of the coils is temperature depended and around $R \approx 0.8 \, \Omega$ at room temperature and at around $R = 1.15 \, \Omega$, when the coils heat up and the power has to be decreased. An estimation of this temperature, when the coils are hot, can be done since the resistance is increasing roughly linear with the factor $\alpha \approx 3.9 \cdot 10^{-3}/^\circ K$. The change in resistance mentioned above corresponds to a temperature of $113^\circ C$.

The design of the coils is chosen to fulfill three purposes. First, the created field has to be sufficiently strong. Field strength around $7 \, \text{mT}$ is aimed for, since this has been used in comparable studies[10].

The field strength of a Helmholtz coil can be solved analytically, but the standard formula uses simplification, that cannot be used for these coils. Independent of the shape of the coils the magnetic field is proportional to the current $I$, which passes though the coils. The drawback of using a high current is a heating of the coils that limits either the field strength or the time the coils can be used at that level until they become too hot. The power that is transformed into heat in the coils increases quadratically with the current as $P = R \cdot I^2$.

The heat could destroy the coils, but the bigger issue is that the cell is also
Figure 3.3: The liquid cell encloses the sample [15].

Heated and the colloid dries out faster. The design of the coils should therefore create a sufficiently strong field with a driving current as small as possible. Secondly, the field has to be homogeneous over the whole volume of the suspension. A field gradient leads to two problems. The nanoparticles in the fluid follow field gradients, so an inhomogeneous field can induce concentration fluctuations in the ferrofluid. Furthermore, the beads would be disturbed by a field gradient of the external field.

Thirdly, the coil design is spatially limited in the frame under the microscope. In the depth (along the axis) the coils are limited by the cell on the inside and by the frame on the outside. The radius of the coils is limited by the lift of the microscope. Also the weight of the coils increases with the size.

To solve the problem of finding an optimal coil design the free software 'FEMM' [16] has been used.

3.3 Sample

All cells have been filled with 25 µl FF, 5 µl magnetic bead dispersion and 2 µl non-magnetic bead solution. Since the non-magnetic bead solution is
more concentrated, the number of magnetic and non-magnetic beads in the cell can be considered as the same.

Each cell has been subjected to a magnetic field for 15 minutes. The field is not constant but switching on and off (as describes in section 3.2) to achieve a higher mobility of the beads. Afterwards, a constant magnetic field has been applied to hold the beads in their positions and around 30 images have been taken in two straight parallel lines crossing the cell perpendicular to the external field. 30 was the upper limit of images that could be taken in the way described within the limitation of the movement of this stage. For some cells the number of images is slightly decreased due to empty regions found in some cells where no image was taken.

**Figure 3.4:** The FEMM simulation shows the magnetic flux density produced by the coils in the sample region.
The ferrofluid (FF) is a water based colloid with magnetite (iron oxide $F_3O_4$) nanoparticles. The particles have a diameter of 10 nm. The particles are encapsulated with a layer of carboxylic acid. The concentration of the used FF is $\rho_{\text{wt.}} = 10\%$ by weight and $\rho_{\text{vol.}} = 3.47\%$ by volume. The magnetic susceptibility is not known for this product. Since the susceptibility is proportional to the FF concentration, it can be calculated from another FF with known susceptibility [17]. This FF has a magnetic susceptibility of $\chi_f = 5.03$ at a concentration $\rho_{\text{vol.}} = 4.5\%$. Since the volume susceptibility is proportional to the fraction of magnetic nanoparticles, the susceptibility of the used FF can be calculated as $\chi_f = \frac{3.47}{4.5} \cdot 5.03 \approx 3.9$

The FF particles are so small that they do not align in an external field. The magnetostatic energy they would gain by aligning is small compared to the thermal energy[18].

The viscosity of the FF is given as $\mu_{\text{vis}} < 50 \text{ cP}$. It is different for each sample, since the original FF is diluted with demineralised water.
The dried FF has been analysed by X-ray diffraction with the Philips Diffractometer "PW3020". The intensity of the Bragg reflections is shown in figure 3.6. The six biggest peaks are marked with the corresponding Miller indices from the lattice planes by which the X-rays are reflected. The Scherrer equation can be used to calculate the diameter of the particles $L$ from the widths of the Bragg peaks as

$$L = \frac{\lambda}{\Delta(2\Theta) \cdot \cos(\Theta)} \quad (3.1)$$

where $\lambda$ is the wavelength of the used X-rays, $\Delta(2\Theta)$ is the full width at the half maximum (FWHM) in radians of the peak at the angle $2\Theta$ and $\Theta$ is the angle of the Bragg beam. The copper anode in the x-ray source produces x-rays with a wavelength $\lambda = 0.154$ nm, which corresponds to the $K\alpha_1$ emission line.

To get the FWHM of each peak, the peaks can be fitted with a Breit-Wigner function:

$$f(x) = \frac{1}{2\pi} \frac{a}{(x-x_0)^2 + \Gamma^2/4} + d \quad (3.2)$$

Figure 3.6: The X-ray diffraction pattern of the dried ferrofluid (grey) is similar to the one of $Fe_3O_4$. The Bragg peaks are marked with the respective Miller indices [19] and are fitted with Breit-Wigner functions (black).
where $a$ is the maximum high of the peak, $x_0$ is the x-value of the maximum of the peak, $\Gamma$ is the FWHM $\Delta(2\Theta)$ of the peak, and $d$ is the background. For small errors the propagation of uncertainty is given as

$$
\sigma(y(x)) = \left| \frac{\partial y(x)}{\partial x} \right| \cdot \sigma(x)
$$

The error for the particle diameter following from the error of $\Delta(2\Theta)$ is

$$
\sigma(L) = \left| \frac{\partial L}{\partial \Delta(2\Theta)} \right| \cdot \sigma(\Delta(2\Theta)) = L \cdot \frac{\sigma(\Delta(2\Theta))}{\Delta(2\Theta)}
$$

The used values and results from the six biggest peaks are shown in table 3.1.

<table>
<thead>
<tr>
<th>Miller index</th>
<th>$2\Theta[\degree]$</th>
<th>$\Delta(2\Theta)[\degree]$</th>
<th>$L$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220)</td>
<td>30.0</td>
<td>0.9 ± 0.2</td>
<td>9.8 ± 2.2</td>
</tr>
<tr>
<td>(311)</td>
<td>35.4</td>
<td>1.0 ± 0.1</td>
<td>8.9 ± 0.7</td>
</tr>
<tr>
<td>(400)</td>
<td>42.9</td>
<td>0.8 ± 0.1</td>
<td>12.4 ± 1.9</td>
</tr>
<tr>
<td>(511)</td>
<td>57.0</td>
<td>1.1 ± 0.2</td>
<td>9.1 ± 1.9</td>
</tr>
<tr>
<td>(440)</td>
<td>62.6</td>
<td>1.1 ± 0.2</td>
<td>9.3 ± 1.3</td>
</tr>
<tr>
<td>(533)</td>
<td>74.1</td>
<td>1.0 ± 0.2</td>
<td>10.9 ± 2.4</td>
</tr>
</tbody>
</table>

Table 3.1: The Scherrer calculations are made for each peak: The used values and results with 95% (1.96$\sigma$) confidence are displayed.

The particle diameter as a weighted mean value from the six evaluated peaks is

$$
L = \frac{\sum L_i/\sigma^2(L_i)}{\sum 1/\sigma^2(L_i)} \pm \sqrt{\frac{1}{\sum 1/\sigma^2(L_i)}}
$$

The resulting particle diameter is $L = (9.4 ± 0.5)$ nm, where the intervall means 95% (1.96$\sigma$) confidence. Additionally, a systematic error is estimated, since peak broadening due to the instrument and distortion in the lattice are not taken into account[20]. Furthermore, a single diameter is calculated, whereas the real particles have a size distribution, which depends on their grade of monodispersity.

The value (10 nm) stated by the producer is within the error intervall of the
calculated particle diameter.

Two types of beads have been used in the samples. Both have the same spherical shape and a diameter of 10 $\mu$m.
The magnetic and non-magnetic beads have two fluorescent dyes to distinguish them. They both absorb light with similar wavelength but emit at different wavelength. The fluorescent emission of both types of beads was

<table>
<thead>
<tr>
<th>wavelength/nm</th>
<th>Pyrromethen non-magn. beads</th>
<th>Propidiumiodid magn. beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>492</td>
<td>495</td>
</tr>
<tr>
<td>Emission</td>
<td>519</td>
<td>639</td>
</tr>
</tbody>
</table>

Table 3.2: Absorption and emission wavelength of the fluorescent dyes that are used to label magnetic and non-magnetic beads.

not sufficiently intensive to be used. Instead the difference in absorption has been used to distinguish them. The magnetic ones absorb the used blue light much stronger and therefore appear dark in the microscope images.

3.4 Analyse Programs

A camera chip on top of the microscope takes images with a resolution of 1392*1040 pixels. The software 'InStudio' controls the camera and automatically adapts the exposure time of the chip to the intensity of the incident light. For the systematic observation 30 pictures for each cell have been taken, which is 2 times 15 pictures over the whole length of the cell perpendicular to the magnetic field.

To analyse these images a MATLAB program has been written based on the free program 'FindCirclesGUI'[21]. The program uses the circular Hough transform to detect the particles and it can distinguish between bright and dark, and therefore between the non-magnetic and magnetic beads.

In the graphical interface important parameters for the image analysis have to be chosen (see figure 3.7). The main reason for this is to distinguish between the bright and dark beads. These parameters have to be adjusted for every cell, since the optics are different. First with higher FF concentrations, more light is absorbed, and the image is darker. Also the light source can move and illuminate each cell in different intensities.
To achieve best settings, for each cell and the set of 30 images, a few (optical characteristic) images are picked to optimise the parameters. The parameters are search-sensibility, threshold, and radii range and are set for bright and dark beads separately. For all bright beads the radii range is $r_b = 8 - 13$ pixels and for all dark beads the range is $r_d = 10 - 15$ pixels. The bright non-magnetic beads appear smaller because only the inner part is bright but the outer ring is dark. Therefore, each of the non-magnetic particles is counted as bright and dark particle and the dark particle positions that fall together with bright particle positions are deleted by the program.

This makes the bright particle sensitivity setting the main tool to distinguish between the particles. If the sensitivity is too high, dark circles are counted as bright and respectively if the value is too low, bright circles appear dark (see figure 3.8). Since all particles are counted as dark circles in the first place the sensitivity for the dark circles influences how many circles are detected at all. A value that is too low results in that beads are not found, while a value that is too big leads to the detection of circles where no bead exist, mainly in the space between other beads.
Figure 3.7: The interface with an analysed image and used parameter. The image shows the detected beads. The parameter for the detection of each type of bead are: sensitivity, threshold, and estimated circle radius in pixels.
After the settings are made, a folder can be chosen and the program finds all JPEG-images inside, analyses them, and stores the particle positions (in units of pixels) and the particle type in text files in a new folder. The extracted information from one image is shown in figure 3.8.

![Image](image_url)

**Figure 3.8:** Top left: Microscope image with magnetic (dark) and non-magnetic (bright) beads, which has some artifacts e.g. from dust on the microscope lens. Top right: Detected circles at a sensitivity $s_b = 0.85$. Left bottom: Detected circles at $s_b = 0.84$, more circles are counted as dark. Bottom Right: Detected circles at $s_b = 0.87$, more circles are counted as white.

A second program can search for these folders. It opens every folder and reads the particle positions.

The way used to analyse the structural arrangement of the beads is to measure the distance between every possible pair of beads. For these pairs it is
distinguished between the three cases: two magnetic ones, two non-magnetic ones and one of each.

The program measures the distance between each pair of beads and stores that distance in a matrix combined with the information of the pair of beads was bright-bright (non magnetic/ non magnetic), bright-dark (non magnetic/ magnetic) or dark-dark (magnetic/ magnetic). To optimize the program speed only small distances of 100 pixels ($d_{\text{count}} \approx 3.57$ bead diameter) are counted. After the distances of every bead to its neighbours is counted, a histogram for each case is created and the distances are sorted into 100 equally sized bins to get a distance distribution. The distribution is normalised to the total number of each bead: magnetic bead, non-magnetic bead and for the magnetic/non-magnetic pair the average number is used.

For the set of 30 images from one cell for each case the weighted (by the number of beads of each type) mean distribution and the weighted standard deviation are calculated.

The final program evaluates the distance distribution of each cell. For the histograms of the magnetic to non-magnetic pairs, the peak, which corresponds to the cubic arrangement, is examined. The height of the peak and the statistical error can be found by using a weighted gauss fit. The Matlab program 'wnonlinfit' [22] is used. For each cell it fits a gauss function for the data, weighted with the inverse squared errors and calculates the error of the fitted parameter.
4

Experiments and Observations

Nine samples with different FF concentrations have been analysed. Table 4.1 displays for each sample: The dilution of the original ferrofluid, the concentration of magnetic nanoparticles by weight, the magnetic susceptibility, the ratio of the FF susceptibility and the susceptibility of the magnetic beads, and the total number of counted bright (non-magnetic) $n_b(n_{nm})$ and dark (magnetic) $n_d(n_{m})$ beads. In the following text and tables the different samples are named by the denominator of the dilution of the used ferrofluid. A total number of around 130,000 beads have been counted in all samples.

<table>
<thead>
<tr>
<th>FF 1/x</th>
<th>conc. wt.</th>
<th>$\chi_f$</th>
<th>$\chi_f / \chi_m$</th>
<th>$n_b(n_{nm})$</th>
<th>$n_d(n_{m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.10%</td>
<td>0.038</td>
<td>0.13</td>
<td>11651</td>
<td>12087</td>
</tr>
<tr>
<td>60</td>
<td>0.13%</td>
<td>0.051</td>
<td>0.17</td>
<td>*3400</td>
<td>*2590</td>
</tr>
<tr>
<td>40</td>
<td>0.20%</td>
<td>0.076</td>
<td>0.25</td>
<td>9104</td>
<td>8781</td>
</tr>
<tr>
<td>30</td>
<td>0.26%</td>
<td>0.102</td>
<td>0.33</td>
<td>4344</td>
<td>3846</td>
</tr>
<tr>
<td>20</td>
<td>0.39%</td>
<td>0.152</td>
<td>0.50</td>
<td>*7305</td>
<td>*12366</td>
</tr>
<tr>
<td>13</td>
<td>0.60%</td>
<td>0.234</td>
<td>0.77</td>
<td>5065</td>
<td>10551</td>
</tr>
<tr>
<td>10</td>
<td>0.78%</td>
<td>0.305</td>
<td>1.00</td>
<td>5472</td>
<td>6383</td>
</tr>
<tr>
<td>8</td>
<td>0.98%</td>
<td>0.381</td>
<td>1.25</td>
<td>12554</td>
<td>8122</td>
</tr>
<tr>
<td>6</td>
<td>1.30%</td>
<td>0.508</td>
<td>1.67</td>
<td>*1801</td>
<td>*4124</td>
</tr>
</tbody>
</table>

Table 4.1: For all samples: FF dilution, weight concentration of nanoparticles, abs. FF susceptibility, relative FF susceptibility, the number of non-magnetic/magnetic beads as sum of counts from 30 images (except FF60: 17 images, FF20: 29 images, FF6: 24 images) are shown.
An overview of images from six different samples is shown in figure 4.1. The images 4.1 a-d show samples with FF susceptibilities $\chi_f < \chi_m$ and on each image cubic arrangement can be observed. In Image 4.1 e) the case where $\chi_f \approx \chi_m$ is shown. A few beads are arranged cubicly but the majority of the magnetic beads are distributed randomly and many of these are isolated from the other beads. In 4.1 f) the case $\chi_f > \chi_m$ is shown. The beads form chains and hexagonal structures. Six samples represent the case.

**Figure 4.1:** The Overview shows characteristic images for different FF weight concentrations/susceptibilities: a) 0.10% ($\approx 0.13\chi_m$) b) 0.20% ($\approx 0.25\chi_m$) c) 0.26% ($\approx 0.33\chi_m$) d) 0.39% ($\approx 0.50\chi_m$) e) 0.78% ($\approx 1.00\chi_m$) f) 1.30% ($\approx 1.67\chi_m$).

where the FF susceptibility is lower than the susceptibility of the magnetic
beads. For this case the magnetic beads have parallel and the non-magnetic beads have anti-parallel effective magnetic moments in relation to the external magnetic field.

The sample FF80 with the lowest FF concentration is shown in fig. 4.2.

In this cell the number of counted beads was the highest of all samples

![Image](image_url)

**Figure 4.2:** Sample FF80, the beads appear are very uneven distributed: a) many images show regions of low bead density, b), c) some images show regions of average bead density, d) many images show regions of high bead density.

with 24,000 beads. The beads are very inhomogeneously distributed in this sample. On the one hand many images with very low density of beads exist as shown in fig. 4.2 a). On the other hand very high densities as in fig. 4.2 d) occur. Only a few images contain a intermediate number of beads (fig. 4.2 b), c)).

In this sample many non-magnetic beads are randomly arranged and isolated from the other beads (4.2 a)-c)), with the exception of the regions with high bead densities (4.2 d)). This can be explained by the low effective susceptibility of the non-magnetic beads.

A much higher FF concentration is used in the sample FF13 as shown in fig. 4.3. In comparison to the sample mentioned above the effective susceptibility
of the magnetic beads is low. Many magnetic beads are isolated and randomly distributed (see fig. 4.3 a)), while the non-magnetic ones are found in chains or hexagonal structures (see fig. 4.3 b)). The total number of beads in this sample is 16,000 and much lower than in the sample FF80, but the beads are more homogeneously distributed (as in fig. 4.3 c), d)).

**Figure 4.3:** Sample FF13: a) very few, isolated, mainly magnetic beads b) mainly non-magnetic beads c) both types, small clusters d) both types, bigger clusters e) both types, inhomogeneous density f) mainly magnetic beads, very inhomogeneous distribution.
5

Discussion

5.1 Structure

The cubic arrangement of magnetic and non-magnetic beads can be observed for all FF concentrations with $\chi_n << \chi_f << \chi_m$. The close packed arrangement of beads of the same kind has been observed in all cells.

The way the particles arrange to reach minimal energy can be observed in figure 5.1. In the figure a composition of two images is shown. The background image is the calculation of the field of four lined up, paramagnetic particles in a homogeneous external field. The semi-transparent image is a detail of a microscope image with magnetic and non-magnetic particles in FF. The field simulation illustrates that magnetic field density is high at the ends of the line and close to the space between two particles. At this positions other paramagnetic particle site. In the second image layer the particles on top of the row are magnetic and arrange at this places.

The field density is lowest on planes perpendicular to the external field, which are at the level of the particle centres. The non-magnetic particles, which site at these positions are seen in the image in the bottom.

In the case $0 < \chi_f < \chi_m$ magnetic beads and non-magnetic beads have anti-parallel effective magnetisations, which leads to cubic arrangement.

For $\chi_f > \chi_m$ both kinds of beads are diamagnetic in the effective system and have therefore parallel effective magnetisations to each other. This leads to hexagonal arrangement. The distance distributions for two samples, which represent these two cases are shown in figure 5.2. In the first case the cubic peak is dominant and in the second case the hexagonal peak.
Figure 5.1: Photo composition of two layers: 1) Simulation of the magnetic flux density produced by a chain of four paramagnetic beads in a homogeneous field 2) Microscope image showing the arrangement of additional beads next to a chain of paramagnetic beads.

Figure 5.2: The distribution of distances between magnetic and non-magnetic beads at different FF susceptibilities: cubic arrangement for $0 < \chi_f < \chi_m$ (red curve) and hexagonal arrangement for $\chi_f > \chi_m$ (blue curve) is observed.
In order to quantify the intensities of the cubic and hexagonal peaks for all samples a weighted Gauss fit has been used (see fig. 5.3). This fits each peak with a Gauss function and determines the peak height $c_1$, the width $c_2$ (in pixels) and the background level/off-set $c_3$. Each evaluated point for the fit is weighted by its error/standard deviation. The results of the fits have errors, which result from the errors of the used data points and of the deviation from a perfect gauss function. In the case of peaks, which are small or close to other ones, this can lead to large errors.

![Figure 5.3: A cubic peak is fitted with a weighted Gauss function.](image)

The results from all samples are shown in fig. 5.4. The dipole force, which creates the arrangement of the beads, can be describes as a product of two factors, where one factor depends on the exact position of the beads and the other one on the FF susceptibility. The plotted function in fig. 5.4 displays the factor of the dipole force that is susceptibility dependend. Since this is only a factor, it can be scaled along the y-axis.

As predicted, the beads arrange cubicly for FF susceptibilities smaller than the one of the magnetic beads; and otherwise hexagonally. The order parameter for the cubic arrangement scales in a similar fashion to the dipole force, which drives the formation of the beads.
Figure 5.4: The measured arrangement is consistent with the theoretical dipole-dipole force.

The negative range for higher FF susceptibility does not mean that the dipole force becomes repulsive, but that the effective dipole moment of the magnetic beads changes from parallel to anti-parallel relative to the external field. In this case both types of beads have anti-parallel dipole moments. For the very low FF susceptibility the hexagonal order parameter is slightly increased. This is explained by the randomly arranged non-magnetic beads. If the beads are randomly, all possible distances between the beads appear and therefore beads in the characteristic hexagonal distance are also found.

5.2 Density of Beads

The density of beads is not homogeneous in every sample as shown in fig. 4.2. The result is that in samples and images with a low number of beads, the number of neighbours of each single bead is lower than in the case of a high number of beads. As a result the total counts in the distance distributions are different. Since for every sample the average distribution of each image
is taken, this leads to a big standard deviation for the mean values. This problem cannot be solved by normalisation by the number of beads, because the beads form clusters. In these clusters the density of beads is higher than the average density and therefore the normalisation by the average density or the total number in the image would give incorrect results. Also the size and shape of these clusters varies for different samples. Therefore, the general cluster size cannot be used for normalisation.

Instead, for each image and for each bead thresholds are chosen. If these thresholds are not fulfilled, the image/the bead is ignored. These thresholds should sort out the extreme cases, but allow enough images and beads to give reliable results. These thresholds should not change the quality of the results, and must therefore be reasonable.

The thresholds regarding the selection of counted images are that images with less than 100 beads and more than 1000 beads in total are not evaluated. This is because in the first case, the bead density is so low, that the single beads are too far away from each other to form clusters. In the second case, the bead density is so high that jamming occurs and structures cannot be formed (see section 5.6). Also images with a total number of beads that differs more than 50% from the average number of beads per image are not counted. This is because the number of neighbours is also depended on the size of the clusters. The smaller the clusters are, the more beads are at the border of the clusters. They have less neighbours than the ones in the middle of the cluster. Therefore, this threshold is chosen, to count images with comparable cluster size.

After the extreme images are discounted, the extreme beads are ignored. In the analyses for every bead the neighbour beads within the radius of 3.57 diameter are counted. Taking into account that closest packing in two-dimensions gives a density of 90%, each bead can have a maximum of 46 neighbours. Since isolated beads should not be counted, a threshold is chosen so that only beads are evaluated with at least 7 neighbours. This is 15% of the maximum possible value. The other extreme is jamming, where the maximum allowed number of neighbours is 41. This is 90% of the maximum possible number.

Aside from the total number of beads, the number of beads of each type can also be inhomogeneous. If a bead of one type is surrounded only by beads of the other type, different structures are formed. Therefore, only beads are counted, where at least 10% and less than 90% of the neighbours are beads of the respective other type.
5.3 Bead Diameter

In the distance distribution the non-magnetic beads appear slightly smaller than the magnetic ones (see figure 5.5). As shown in table 5.1 the distances between non-magnetic neighbour beads are mainly smaller than the distances between magnetic neighbour ones. The difference is bigger in the samples with higher FF susceptibility. This can be explained by the higher attractive force between the beads in these cells. Over all samples the distances between direct neighbouring non-magnetic beads are 3.9% smaller. For second neighbours these are 3.6% smaller. The size difference between the two types of beads could change the created structures. In literature in experiments with very similar beads, bigger size differences for have been observed as in the order of 10% in the work of Khali et al. [10].

Direct measurement of the size of the beads from the images is not possible, since the optical properties are too different.

<table>
<thead>
<tr>
<th>FF conc.</th>
<th>$D_{\text{non-mag.}}/D_{\text{mag.}}$ 1st</th>
<th>$D_{\text{non-mag.}}/D_{\text{mag.}}$ 2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.01</td>
<td>1.00</td>
</tr>
<tr>
<td>60</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>40</td>
<td>0.98</td>
<td>0.97</td>
</tr>
<tr>
<td>30</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>20</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>13</td>
<td>0.93</td>
<td>0.94</td>
</tr>
<tr>
<td>10</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td>8</td>
<td>0.94</td>
<td>0.97</td>
</tr>
<tr>
<td>6</td>
<td>0.95</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 5.1: Ratio of distances (of first and second neighbours) between non-magnetic beads and distances between magnetic ones.

Figure 5.5: The distances between the non-magnetic beads (full line) are smaller than the distances between the magnetic ones (dashed line).
5.4 **Viscosity**

The ferrofluid has a much higher viscosity than water. A high viscosity leads to a lower mobility of the particle. If only the magnetic potential energy is considered the non-magnetic particles would align best in the highest concentrated FF. Due to the viscosity of the ferrofluid this maximum can be shifted to lower concentrations where the non-magnetic particles still have enough effective dipole moment, but a higher mobility due to the lower viscosity of the surrounding medium.

Another issue that comes with different viscosities is the particle distribution of the beads. A drop of FF with dispersed beads drags the beads with it, while it is squeezed between the plates of glass. A higher diluted suspension has a lower viscosity and when squeezed between the glass, the FF will move to the sides, while the beads remain behind. This can lead to a less homogeneous bead distribution (as shown in 4.2).

5.5 **Lattice Defects**

Lattice defects reduce the degree of crystallisation. After structures have formed to some degree, the extension of these structures reduces the mobility of the beads. A chain of particles in horizontal direction prevents the movement of free beads vertically. Vacancies between two layers can therefore not be filled (see figure 5.6 a). Another issue is the transition between different structures. One layer introduced between two other layers of different beads creates two transitions effects. The transition from two to three parallel layers and from hexagonal (at the side with two equal layers) to cubic (at the side with the introduced layer), is shown in figure 5.6 b.

![Figure 5.6: Vacancies (a) and introduced layer in cubic lattice (b) are examples of lattice defects that are found in the samples.](image)
5.6 Jamming

Another observed phenomenon is jamming. Jamming or crowding describes the loss of mobility of particles with increasing density in granular media, colloidal suspensions or molecular systems [23].

In regions with a high density of beads the beads are mainly close-/hexagonal packed or randomly ordered. This can be seen in figure 5.7. The beads do not have enough place to create a cubic structure and their mobility is too low to arrange in a structure with low magnetostatic potential energy.

Figure 5.7: Jamming occurs at high bead densities.
Conclusion and Outlook

The goal of this thesis was to discover how magnetic and non-magnetic beads, dispersed in a ferrofluid, arrange in a homogeneous in-plane magnetic field. Nine samples have been prepared and analysed and it has been found that magnetic and non-magnetic beads form either cubic or hexagonal lattices depending on the susceptibility of the ferrofluid in relation to the susceptibility of the magnetic beads. The appearance of different lattices is explained by minimisation of magnetostatic energy. Furthermore, the degree of how much the beads arrange in the lattices is described by a dipole-dipole force. The observed structures from the experiments are in agreement with the theoretically expected results. The results from this thesis are consistent with previous research from other groups and extend the knowledge about these systems for the case of in-plane fields.

In this project it has been observed how non-magnetic beads get effective magnetic behaviour, and which structures are formed. This can be used in further experiments to give non-magnetic particles with other properties, like conduction, an effective magnetic moment. Because this will make it possible to combine magnetic behaviour with other properties, this will make it possible to create completely new systems. The system analysed in this thesis exhibits a number of interesting aspects. Many variations of parameters are possible with completely different, new results, in which further investigations could follow.

One parameter that can be changed is the field direction. On the one hand, in this thesis a in-plane external field were used and phase transitions with the variation of the FF concentration are described. On the other hand,
a out-of-plane field was used in literature [5], where phase transitions with the variation of the ratio between magnetic and non-magnetic beads are described. An interesting continuation of this research would be to apply a superposition of in-plane and out-of-plane fields. Furthermore, beads with different radii could be used and newer finding show that structures like rings can be created in this case [5].

In this thesis the ferrofluid concentration has been varied over the whole range of interest, but for every concentration a new cell has been created. At some concentrations cubic structures with alternating layers of magnetic and non-magnetic beads appeared and at some concentrations hexagonal structures with random kinds of beads have been found. New structures could be created in a flow cell, where the FF concentration could be varied. The initial concentration could create alternating cubic layers and with the change in concentration these layers could change into hexagonal packing without losing the alternating magnetic/non-magnetic layers.

While in this thesis beads in the micrometer scale have been used, it is also possible to investigate the assembly of smaller particles like the FF nanoparticles. These nanoparticles should not be assembled at room temperature [18] except close to surfaces [24]. Another completely different set of possibilities comes with the use of dynamic fields. In recent research it has been found that under the right conditions magnetic beads in dynamic field can self assemble to self propelled 'swimmers' [25].

A phenomenon which has been observed within this project is jamming. When the bead concentration is too high the beads stop moving due to jamming. This could be analysed by pulling a magnetic bead through a cluster of non-magnetic beads. The advantage of this system is that through the magnetic interaction a very constant force can be applied.

Finally with the use of colder fluid (e.g. liquid nitrogen) the Brownian motion can be reduced and smaller particles can be used. At this temperature the FF nanoparticles can be structured. Since in this size there is no magnetic medium any more there is no way to make non-magnetic particles behave diamagnetically. The only materials with high diamagnetic susceptibility are superconductors. Since cold liquids are already required to reduce the Brownian motion, it could be a viable choice to use superconducting nanoparticles. If a mixture of superconducting and paramagnetic particles is used, it could be possible to produce, the same structures as described in this thesis.
Bibliography


Acknowledgement

I would like to thank my supervisors Max Wolff and Vassilios Kapaklis for starting and shaping this project and for all the help with the whole project, the motivation, the interesting discussions and the writing of this report.

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Finally I thank my family Carsten, Doris, Hella and Maria for their support and Mark Meachen who helped me a lot with the corrections.
Appendix A
Figure A.1: LabView program for coil current control: The resulting current in the coils is plotted in fig. A.2. LabView controls the power supply by the USB device "NI USB 6009". Since this device has no internal clock, the LabView program has to use a software generated timer. This means that the code performs in each loop only one step. Since 150 loops (steps) per second can be performed, the device is able to produce a smooth square-wave current with the aimed frequency of 0.33 Hz used in the experiment. A square-wave function has hard edges, which could cause high inductive resistance in the coils. Therefore a digital filter for high frequencies is used in the code to smooth the signal.
Figure A.2: A smoothed square current in the LabView window: The current is reduced every 3 seconds. The high current level corresponds to 10 Ampere.