Magnetically governed self-assembly of soft matter

A look into interfacial layering, crystallization and percolation

APURVE SAINI
Abstract

Self-organisation is the key route for assembling colloidal particles into well-defined structures. Decisive for this are the interactions between the constituents, which are amongst others steric, electrostatic or magnetic. A deep knowledge on the underlying physical processes during self-assembly is crucial for the design and fabrication of well-defined hierarchical architectures from a nanometer scale as well as for realizing smart, functional or stimuli responsive synthetic materials. In this dissertation, the self-assembly of colloidal magnetic particles into organized and multi-layered structures is studied. Particular emphasis is given to solid-liquid boundaries and the response to applied magnetic fields. Particle coatings with specific functional molecules stabilize the nanoparticles (NPs) in the solvent and can simultaneously promote their assembly at a substrate. An example in this context is N-hydroxysuccinimide interacting with (3-aminopropyl)triethoxy silane at the substrate. As a result of this chemical affinity, uniform and densely packed particle wetting layers are seeded which then instate the layering process. As an alternative to chemical binding, the magnetic stray field of a ferrimagnetic (Tb$_{15}$Co$_{85}$ film) deposited on a substrate induces particle self-assembly with dense layers as well. The application of an external magnetic field further promotes densification, particle layering and leads to variations in the assembly characteristics such as quasi-domain formation of closely packed layers. At an interface with a magnetic field applied in the plane of the interface, Brownian motion and Neel relaxation of the NPs are decisive for the layering and give raise to these domains. For a magnetic field oriented along the surface normal similar structural layering but denser packing is found. The self-assembly is a relatively slow process and evolves over hours and is maximized, most ordered and dense for superparamagnetic NPs which are single domain and having a large remanent moment and reduced thermal mobility. Small quantities of magnetic micelles in a hybrid magnetic polymer nanocomposite, facilitate the crystallization of Pluronic F127 micelles dissolved in water into single crystalline structures via a micro-shear effect under applied magnetic field. Also, a magnetic field applied to a colloidal dispersion of conducting magnetic and non-magnetic polystyrene microbeads suspended in an oil-based ferrofluid can lead to percolated structures. This allows current transmission and switching. A working contact for possible applications in automotive, switchboard and telecommunications is demonstrated.

Keywords: Self-assembly, Soft matter, Colloids, Magnetic nanoparticles, Ferrofluid, Solid-liquid interface, Neutron reflectometry, Electrical sensing, Microcontact

Apurve Saini, Department of Physics and Astronomy, Materials Physics, 516, Uppsala University, SE-751 20 Uppsala, Sweden.

© Apurve Saini 2020

ISSN 1651-6214
ISBN 978-91-513-0957-6
urn:nbn:se:uu:diva-409494 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-409494)
Dedicated to my wife, Natasha
List of Papers

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


VI. Saini, A., Kapaklis, V., Wolff, M. Magnetically controlled electric current through a colloid. *Manuscript*


Reprints were made with permission from the respective publishers.
Comments on my participation

I. Planning and performing experiments, sample preparation, data analysis and responsible for writing the majority of the manuscript.

II. Planning and performing experiments, sample preparation (apart from synthesizing the particles), participation in data analysis and interpretation and contribution in writing the manuscript.

III. Planning and performing experiments, sample preparation, data analysis and responsible for writing the majority of the manuscript.

IV. Planning and performing experiments, sample preparation, data analysis and responsible for writing the majority of the manuscript.

V. Planning and performing experiments, sample preparation, data analysis and responsible for writing the majority of the manuscript.

VI. Planning and performing experiments, sample preparation, data analysis and responsible for writing the majority of the manuscript.

VII. Performing experiments, sample preparation, contribution in writing the manuscript.

VIII. Contribution in writing the manuscript.
Contents

1. Self-assembly in magnetic liquids ............................................................ 11

2. Magnetic materials, colloids and self-assembly ....................................... 14
   2.1. Magnetic materials ............................................................................ 14
   2.2. Magnetic colloids and ferrofluids ...................................................... 15
   2.3. Interactions in magnetic colloids....................................................... 16

3. Colloidal particles and solid substrates ..................................................... 20
   3.1. Nanoparticles: Synthesis and characterization .................................. 20
   3.2. Substrates: Surface functionality ....................................................... 23
       Piranha treated silicon substrate ......................................................... 23
       Silanized silicon substrates ............................................................... 23
       Magnetic substrate with perpendicular anisotropy .............................. 25

4. Neutron scattering techniques for investigating colloidal particle assembly at silicon interfaces .................................................................. 27
   4.1. Neutron reflectivity ........................................................................... 28
   4.2. Off-specular scattering...................................................................... 32

5. Scattering experiments and data analysis .................................................. 34
   5.1. Liquid cell for neutron reflectivity .................................................... 34
   5.2. Reflectivity experiments.................................................................... 35
   5.3. Layer model for reflectivity data fitting ............................................ 36

6. Assembly of magnetic nano-particles at solid substrates .......................... 38
   6.1. Tuning of micellar self-assembly with magnetic particles............... 38
   6.2. Self-assembly of magnetic particles at modified silicon substrates .40
   6.3. Self-assembly of magnetic particles with different size ................. 42
   6.4. Magnetic particle assembly in an out-of-plane magnetic field...........44

7. Ferro-fluids applied as electrical contacts ................................................. 51
   7.1. Concept of effective moments and experimental setup............... 51
   7.2. Current transmission and switching performance ........................... 53

8. Summary and Outlook .............................................................................. 57

Svensk sammanfattning ................................................................................ 59

Acknowledgments.......................................................................................... 61

References..................................................................................................... 63
Abbreviations

APTES (3-aminopropyl)triethoxysilane
FF ferrofluid
MFM magnetic force microscopy
NHS N-hydroxysuccinimide
NP nanoparticle
NR neutron reflectivity
OTS octadecyltrichlorosilane
PEO polyethylene oxide
PF127 Pluronic F127
PNR polarized neutron reflectivity
PPO polypropylene oxide
SEM scanning electron microscopy
SLD scattering length density
SANS small-angle neutron scattering
TEM transmission electron microscopy
1. Self-assembly in magnetic liquids

The ascent of soft matter from a subaltern to mainstream discipline of physics is related to the promise of unraveling the ‘enigma’ of self-assembly, an endeavor which if realized, could enable large-scale engineering of complex structures with broad societal and economic impact [1, 2]. The strong tendency in soft matter materials to form complex and hierarchical structures is related to the comparable weak binding energies, which are on energy scales of $k_b T$ ($k_b = $ Boltzmann constant, $T = $ temperature) at room temperature [3]. Another consequence of this weak binding are interesting material properties as we experience in some of the materials we use on a daily basis for instance, lubricants, paints and cosmetics. These are difficult to categorize as solid, liquid or gas, since, for example their elastic and viscous properties may lie in between those of a liquid and solid. Soft materials can be deformed or structurally altered by thermal, magnetic or electrical forces, and show a large, slow and non-linear response compared to a liquid or a solid [4]. Moreover, soft matter can be single phase, like e.g. polymers, or multiphase, as colloidal dispersions or aerosols etc. In the latter case, the components can interact with each other or their medium to spontaneously form hierarchical structures as the system evolves towards equilibrium [4]. Their equilibrium properties exhibit a rich diversity, due to the many-body nature of interactions (electrostatic, magnetic or steric) [5-7]. Thus, colloidal dispersions can serve as simple models or building blocks for research on self-assembly [8-10]. These dispersions allow the study of self-assembly of particles by shear [11], optics [12], depletion interactions [13], sedimentation [14] as well as magnetic [15] and electrical fields [16]. Further, the structures and dynamics resulting from tunable interactions between individual particles can be studied in real space. Therefore, smart (stimuli-responsive) soft matter can be realized by including components which are sensitive to the chemical environment or to external fields.

The thesis is privy to magnetic soft matter so-called magnetic colloids, which are carrier fluids such as, oil or water in which magnetic nanoparticles (NPs) are dispersed. These are nano-scale building blocks that follow magnetic field gradients [17]. Further, the particles offer tunability as their surface can be functionalized with molecules and be manipulated contact-less with magnetic fields. Directed self-assembly can be achieved by magnetic fields triggering a prompt, anisotropic and reversible response resulting from the magnetic interactions [18, 19]. This may result in 1D [20], 2D [21] and 3D
ordered structures such as linear or branched chains as well as clusters with tunable degree of crystallinity. Understanding the collective interactions of dissolved magnetic NPs, their self-assembly on surfaces and the influence of external magnetic fields are of interest from a fundamental perspective and for applications such as, medical imaging [23], drug delivery [24], photonics [25], and data storage [26].

A.T. Skjeltorp in 1984 [27] and more recently Cartensen et al. [28] showed that a magnetic colloid can be used as a medium to tune the magnetic properties of micrometric particles (beads). In this work, conducting microscopic paramagnetic and diamagnetic polystyrene beads dispersed in an oil-based magnetic colloid were subjected to external magnetic and DC electric fields to explore the formation of percolated structures. Questions such as weather the current is magnetically tunable, can be scaled to become suitable for modern applications such as in automotive and telecommunication and offer possibilities for developing future electrical switches, are answered. See papers V and VI for details.

Important for a good contact is the interface between a solid and the colloid. The self-assembly of colloidal magnetic NPs at an interface with a solid silicon surface was studied by Vorobiev et al. in 2004 in a horizontal geometry [29]. It was shown by neutron reflectometry (NR) measurements that the direction of external magnetic field influences the particle assembly as well as the ordering at the interface. Under an in-plane field, short range ordering and under out-of-plane field, long range ordering was reported. Gapon et al. [30] in a similar study utilized two kinds of magnetic colloids, first, a colloid with magnetic NPs coated by a double layer of sodium oleate, and second, a colloid with cobalt ferrite NPs stabilized by lauric acid/sodium n-dodecylsulphate. The authors reported the formation of just one single adsorption layer for both colloids. Complimentarily, an interface can provide a template for the targeted self-assembly and layers may be deposited in a very controlled way. In this context, magnetically structured substrates have been used to study the guided crystallization of colloidal particles [31-33].

The self-assembled nanostructures adsorbing onto the interface are useful for designing multidimensional nanocrystalline structures capable of demonstrating remarkable collective properties compared to isolated single NPs. For the construction of these NP systems, the interaction of the first layer (wetting layer) with a substrate is of great importance, since, it forms the seed layer for structures grown above. One way to achieve a uniform and dense wetting layer is by enhancing the affinity between the colloidal particles and the solid wall, e.g., by the formation of chemical bonds. In addition, the functional group facilitates water dispersibility which is crucial for e.g., biological applications [34]. Two efficient methods for phase-transfering the as-synthesized magnetic particles to an aqueous phase are, (a) particle coating with hydrophilic functional molecules such as N-hydroxy succinimide (NHS) offering carboxyl (-COOH) terminal groups [35] or (b) coating with a polymer such as pluronic
F127 (PF127), which is a triblock copolymer ((ethylene oxide)$_{99}$-(propylene oxide)$_{65}$-(ethylene oxide)$_{99}$) [36]. It exhibits an amphiphilic behavior in aqueous solution, and for elevated temperatures and/or copolymer concentrations forms micelles with hydrophobic core and hydrophilic shell [37]. PF127 coating over magnetic NPs results in the formation of magnetic micelles.

This dissertation describes the assembly of magnetic NPs at solid interfaces with controlled interactions between the particles and the substrates, and by the application of magnetic fields. Using NR, it is shown that densely packed layers form. Their structure is defined by the templated substrate and wetting layer, and mediated by long-range magnetic dipolar forces. The interactions between NHS coated NPs and the solid surface in particular was initiated by providing amine functionality to the surface, i.e., chemical deposition of a monolayer of 3-Aminopropyltriethoxy silane (APTES) on the solid surface [35] (paper II, III). As an alternative coating, a ferrimagnetic film of amorphous TbCo sputtered on a silicon surface [38] is described as a magnetic template layer for the particle assembly. The film with strong perpendicular anisotropy eliminates the need for a chemical bond between the magnetic NPs and the surface (paper IV). Moreover, it is shown how the self-assembly of micellar crystals at interfaces can be tuned and manipulated by the addition of small quantities of magnetic particles as a result of micro-shear (paper I).
2. Magnetic materials, colloids and self-assembly

Colloidal self-assembly is determined by the interactions between the building-blocks. This chapter gives a short overview of relevant concepts. Further, the structure, dynamics, and tuning parameters of magnetic colloids, with emphasis on the magnetic interactions within as well as with a solid boundary are introduced.

2.1. Magnetic materials

Magnetic properties in materials are characterized by the response to an external magnetic field [39]. An important measure is the magnetic susceptibility \( \chi \), which is the ratio of the magnetization \( M \) of a material to the applied field \( H \). The following material classification is made:

For diamagnetic materials, the magnetic susceptibility is negative and the induced magnetic moment is anti-parallel to the applied field [39]. Most materials, including water, copper, silicon, diamond, proteins, DNA, polymers, glasses etc., are weakly diamagnetic, with \( \chi \) on the order of \(-10^{-5}\).

Ferromagnetic materials such as iron, cobalt and nickel show a remanent magnetization for temperatures below the Curie temperature [39]. The strong exchange coupling between the atomic moments leads to ferromagnetism. Such materials are characterized by the formation of magnetic domains, regions of atomic moments that are aligned parallel to minimize the exchange energy. The net magnetic moment within a domain is the summation of the atomic moments. In an external field, the magnetic domains align along the field. At the saturation field, all domains are aligned and the magnetization is maximized. Above, the Curie temperature, the materials become paramagnetic.

Paramagnetic materials such as platinum, potassium & oxygen are characterized by a small and positive magnetic susceptibility \( \chi_m > 0, 10^{-5} \) to \( 10^{-3} \) [40]. For a given temperature, the magnetic response of such materials is a function of the applied field. If the field is small the magnetic response is linear. If the applied field is large, the magnetization reaches saturation. This is
because the permanent magnetic moments of atoms in the material are randomly oriented with the net magnetization being zero but may become aligned in an externally applied field.

In superparamagnetic materials, the individual atomic moments result in a net magnetic moment which randomly orientates due to thermal fluctuations. If an external field is applied, the moment aligns along the field direction resulting in a large magnetization [39]. When the field is removed, the moment loses alignment and the magnetization vanishes [41]. The difference to paramagnetism is that the net magnetic moment aligns more easily with respect to the external field. This results in a much larger susceptibility, with no coercivity or remanent magnetization.

2.2. Magnetic colloids and ferrofluids

Ferrofluids (FF) are stable colloidal dispersions of magnetic NPs, e.g. of magnetite (Fe₃O₄), stabilized with organic surfactants like oleic acid or oleylamine and dispersed in a carrier fluid such as oil, water or kerosene. A schematic of a ferrofluid is sketched in Fig. 1. The choice of solvent (organic or water) depends on the polarity of the surfactant. For hydrophilic terminations, the particles are stable in water. Thermal agitation of the particles keeps them suspended in the liquid and the molecular coating prevents agglomeration. Once a magnetic field is applied, a force along the field gradient is exerted on the particles and the liquid becomes macroscopically deformed. Stability as a uniform suspension is an important property of FFs that most commercial applications require [42]. This stability is dictated by the size of the particles, which needs to be sufficiently small to prevent sedimentation due to gravity. Charge and surface chemistry contribute to stability by providing coulombic [43] and steric repulsion [44] among the magnetic NPs. Fig. 1 also illustrates the anisotropic response of a FF to an applied magnetic field. In a field, the magnetic moments of the particles become aligned, resulting in the formation of chains along the magnetic field lines.
2.3. Interactions in magnetic colloids

The thermodynamic equilibrium structure of colloidal particles is defined and can be predicted from the interactions among them. In the simplest scenario, they interact only via hard-core repulsions. For purely hard particles, the potential energy of the system is not affected by the positions of the particles. So, any phase transition that occurs in such a system is driven by entropy. The colloidal particles may also interact with each other through different short- and long-range forces. For example, the short-range attractive Van der Waals force drives the aggregation of colloidal particles when they come close to each other [45]. The force increases with the moment of the NPs.

The magnetic properties of NPs can be categorized with respect to their size [46,47]. NPs above a critical diameter, $d_{cr}$, (for example, ~30 nm for single crystalline Fe$_3$O$_4$ [48]) for the formation of domains are multi-domain and display coercivity as well as remanent magnetization [49]. The magnetization reversal takes place via domain wall motion. Below $d_{cr}$, the formation of domains is not energetically favorable and the particles are single domain [50]. If suspended in a liquid, they show a collectively superparamagnetic behavior since the moments can reorient by rotation of the particle itself (Brownian relaxation) into the field direction [51]. For particles with diameter lesser than $d_{spm}$ (superparamagnetic limit), the magnetic anisotropy energy becomes
comparable to thermal energy [52]. As a result, the particles spontaneously change the magnetization direction (Néel relaxation). These particles are intrinsically superparamagnetic [53, 54] (for example, $d_{spm}$ in Fe$_3$O$_4$ NPs is below 15 nm [47]).

Apart from Van der Waals force, another attractive interaction specifically between the NPs in the FF is the magnetic dipole–dipole interaction. For a spherical particle with moment $\vec{m}$, the magnetic field of the particle at the position of second particle is given by $\vec{H}_1 = [3(\vec{m} \cdot \vec{r})\vec{r} - \vec{m}] / l^3$, where $l$ is the centre-centre distance between the two particles and $\vec{r}$ is the unit vector parallel to the line connecting the two centers. The dipole-dipole interaction energy of the second particle ($U_2$) with the same magnetic moment is given by $U_2 = (3\cos^2 \phi - 1)|\vec{m}|^2 / l^4$, where $\phi$, ranging between $0^\circ \leq \phi \leq 90^\circ$, is the angle between the direction of external magnetic field and the line connecting the centers of the two particles. The dipole force exerted on the second particle induced by the first particle can be expressed as $F_2 = 3\vec{r}(1 - 3\cos^2 \phi)|\vec{m}|^2 / l^4$. This expression clearly shows the dependence of the dipole-dipole force on the configuration of the two dipoles. At the critical angle of $54.09^\circ$ the interaction is zero. The dipole-dipole interaction is repulsive when $54.09^\circ < \phi \leq 90^\circ$ (Fig. 2, left) and attractive when $0^\circ \leq \phi < 54.09^\circ$ (Fig. 2, right). When the interaction energy is larger than the thermal fluctuations, the magnetic dipole-dipole force drives the self-assembly of particles into 1D chains along the field lines [55]. Further, since the force on a particle is proportional to the field gradient, the dipolar interactions result in the particles moving towards larger flux densities [68].

![Fig. 2. For colloidal particles in a magnetic field, the repulsive (left) and the attractive (right) dipole–dipole forces (gray arrows) in different particle configurations drive the formation of chains along the magnetic field lines. The white arrows indicate the induced dipole moments of the particles aligned in the direction of the external magnetic field (indicated by the black arrow).](image)

In the absence of an external magnetic field, the formation of particle structures is primarily defined by magnetic dipolar interactions [19, 20]. However, in a colloid with magnetic particles of sizes below $d_{cr}$, the thermal energy dominates and the magnetization is flipped easily. The resulting system is thus superparamagnetic and the particles can easily be stabilized in a colloid solution because the magnetic dipole-dipole interactions between them are small. The total attractive force between two NPs in a colloid is the sum of their Van
der Waals and magnetic dipole–dipole interaction forces. Therefore, the colloidal stability has to be ensured by additional repulsive interparticle interactions (steric repulsion). This is realized by grafting an organic (surfactant) layer onto the particle which acts as a steric barrier against agglomeration. Magnetic NPs such as magnetite are often synthesized in aqueous solvents by coprecipitation [57, 58]. A disadvantage of this route is a poor control of size. In contrast, the NPs synthesized using solvothermal routes are highly uniform in all respects (size, shape, composition, and crystallography) [59, 60]. Unfortunately, the surfactant coating (typically oleic acid) on the as-synthesized NPs renders them insoluble in polar solvents like water. These particles synthesized in non-polar organic solvents have carboxyl groups (-COOH) attached to the surface and the less-reactive methyl groups (hydrophobic, -CH3) oriented towards the solvent (Fig. 3, left). Therefore, highly monodisperse magnetic NPs are generally synthesized in organic solvents and then phase transferred to aqueous solvents using surface functionalization [61, 35].

One particle functionalization is achieved with 1-Ethyl-3-[3-dimethylaminopropyl]-carbodiimide hydrochloride (EDC). This is a water soluble zero-length crosslinking agent which reacts with carboxyl groups on the NP surface to form very reactive and highly electrophilic, O-acyl isourea intermediates, (Fig. 3, middle). This activation of the carboxyl groups makes them very reactive towards nucleophilic reagents (such as primary aliphatic amines). To increase the stability and reaction rate of the active intermediate, an additional coupling reagent N-hydroxysuccinimide (NHS) is included in the process (Fig. 3, right), which results in the formation of an amine reactive NHS ester.

![Fig. 3. EDC reacts with a carboxylic-acid group on Fe3O4 NP surface forming an amine-reactive intermediate which may react with an amine on the silicon surface but is unstable. The addition of NHS stabilizes the intermediate by converting it to an amine reactive NHS ester.](image-url)
Another method for phase transferring the synthesized NPs to water is by using PF127 as a phase transfer agent. The hydrophobic PPO chains assemble onto the hydrocarbon tails of the oleic acid layer via hydrophobic interactions [62], providing a high yield of NPs coated with PF127, see schematics in Fig. 4. PF127 coatings render these magnetic NPs biocompatible [63]. After the phase transfer, the NPs remain superparamagnetic with saturation magnetization $\sim 96\%$ of the maximum theoretical value [64].

**Fig. 4.** Schematic for a water dispersible magnetic NP coated with PF127. The hydrophobic subunit from the copolymer adsorbs onto the oleic acid with hydrophilic subunits being the terminal groups in water.
3. Colloidal particles and solid substrates

The assembly of colloidal magnetic NPs for example close to different substrates or into percolated structures is discussed below. This chapter describes the characteristics of the NPs as well as the substrates.

3.1. Nanoparticles: Synthesis and characterization

Fe$_3$O$_4$ NP samples (FF5, FF15 and FF25) functionalized with NHS ester (activated, dry-stable form) were purchased from Sigma Aldrich. The morphology and size of the FF NPs was verified by transmission electron microscopy (TEM). For TEM sample preparation, a carbon-coated 200-mesh copper specimen grid (Agar Scientific Ltd. Essex, UK) was glow-discharged for 1.5 min. One drop of the diluted sample solution was deposited on the grid and left for 2 min. Excess fluid was removed with a filter paper. The grids were then air-dried at room temperature and examined. Images are shown in Fig. 5 for the three samples having an average diameter of 4.1(5) nm, 14.9(6) nm, and 22.2(11) nm, respectively. Parameters were extracted from their number and the square root of the particle area in the image by utilizing ImageJ freeware [65]. The spherical nanocrystals are highly uniform in size.

![TEM images of FF samples FF5, FF15 and FF25 comprising of Fe$_3$O$_4$ NPs coated with NHS. The scale bars are 50 nm. Images reproduced from paper IV.](image)

Particle form factors were extracted using small angle neutron scattering (SANS) performed on the NGB30m SANS instrument at the NIST Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST) in USA. The NP dimensions determined by fits are tabulated in Table 1 and in line with the ones from the TEM measurements.
Table 1: NP dimensions extracted from SANS.

<table>
<thead>
<tr>
<th></th>
<th>FF5</th>
<th>FF15</th>
<th>FF25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core diameter [nm]</td>
<td>3.2(2)</td>
<td>15.4(2)</td>
<td>21.3(2)</td>
</tr>
<tr>
<td>Shell thickness [nm]</td>
<td>6.4(2)</td>
<td>4.9(1)</td>
<td>6.9(1)</td>
</tr>
</tbody>
</table>

PF127 functionalized Fe$_3$O$_4$ NPs were synthesized with 0.5 mmol iron (III) acetylacetonate [Fe(acac)$_3$] as precursor, 0.5 mmol oleic acid and 0.5 mmol oleylamine as surfactants, and 4 mmol 1,2-hexadecanediol (1,2-HDD) as reducing agent, mixed in 70 mL of benzyl ether solvent. The mixture was stirred for an hour and transferred to a teflon-lined autoclave where it was kept at 180 °C for 3 days before cooling to room temperature. The resultant was a black-colored solution indicating the formation of Fe$_3$O$_4$ NPs. The solution was then precipitated by 50 ml ethanol and centrifuged at 12000 rpm for 15 min. Later hexane was added for redispersion. The phase transferring to an aqueous solvent was carried out with 5 mL of 10 mg/mL hexane dispersion of as-synthesized NPs being mixed with 10 mL of 500 μM solution of PF127 in 10× conc. phosphate-buffered saline at 6 °C for 1 h. The solution was then dried under an argon gas flow overnight to obtain water dispersible NPs. Unbound PF127 was removed by dialyzing the NP solution against 1 L D$_2$O with a cellulose membrane (molecular weight cutoff: 25 kDa) for 48 h. Agglomerated particles, if any, were removed by filtration.

A macroscopic test was performed to observe particle solubility in water before and after functionalization with PF127, see photographs in Fig. 6 (top row). Before functionalization, the oleic acid coated particles are in the organic phase. After functionalization, the particles are in the water phase. TEM images of oleic acid functionalized NPs having diameter of 10.6(5) nm, before and after functionalization with PF127 are shown in Fig. 6 (bottom row). The particles are monodisperse both in hexane and water. There was no significant change in the size/shape of the particles and no sign of agglomeration after phase transfer.
Fig. 6. (Top row) Photographs showing oleic acid coated iron oxide particles insoluble in water. After functionalization with PF127, the particles are soluble in water. (Bottom row) Corresponding TEM images showing that after phase transfer the particles retain their morphology and do not agglomerate.

The hydrodynamic diameter and the organic coating of the NPs were studied before and after the phase transfer by dynamic light scattering (DLS). The measurement was carried out in a Zetasizer Nano-ZS (Malvern Instruments Corp.) at 27 °C in polystyrene cuvettes with a path length of 10 mm. The hydrodynamic diameters were extracted using the Stokes–Einstein relation [66]. For all the measurements, the samples were diluted in deionized water to ~0.01 mg/mL and sonicated using a water bath sonicator for 10 min. The DLS results show that the average hydrodynamic diameters of oleic acid@Fe₃O₄ NPs are 13.0(6) nm (PDI = 0.21) and 37.5(21) nm (PDI = 0.22). These increased to 36.0(9) nm (PDI = 0.26) and 71.6(14) nm (PDI = 0.32), respectively, for F127@Fe₃O₄.

Spectroscopic analysis of the coatings was carried out on a PerkinElmer instrument, Spectrum One ATR-FTIR. The infrared vibration spectra of PF127 and F127@Fe₃O₄ are shown in Fig. 7. In both samples, the Pluronics show very intense peaks close to 1107 cm⁻¹ [64]. The peaks related to oleic acid were observed at 1720 cm⁻¹, 2841 cm⁻¹ and 2893 cm⁻¹ [67]. The peaks from both oleic acid and PF127 were clearly identified in the spectrum of PF127 coated NPs, indicating the presence of both molecules on the particle surface.
3.2. Substrates: Surface functionality

In the present work, the solid surface was modified in order to investigate the influence of variations in surface energy on the self-assembly of colloidal NPs.

Piranha treated silicon substrate

Piranha solution is a 70:30 mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂), and is used for etching the substrates. The mixture being a strong oxidizing agent removes even trace amounts of organic matter and hydroxylates most surfaces, making them highly hydrophilic [68], with a OH termination. For the treatment, a silicon wafer (with native SiO₂) was immersed (polished side up) into a freshly prepared Piranha solution kept in a thoroughly cleaned PTFE beaker for 30 minutes. The wafer was then placed in boiling ultrapure water for 20 minutes and thereafter, kept in ultrapure water until needed. After treatment, a contact angle for water of 6° was measured.

Silanized silicon substrates

Organosilane self-assembled monolayers (SAMs) are obtained using self-assembling molecules. They consist of an anchoring group with a strong preferential adsorption to the substrate, an alkyl chain and a terminal functionality.
The SAMs prepared on smooth surfaces like silicon wafers exhibit extraordinary properties such as chemical homogeneity, ultra-low surface roughness and controlled wettability [69]. The latter can be varied from hydrophilic to hydrophobic, depending on the head group. Silane layers are mechanically robust [70], thermally stable up to at least 250 °C and are not subject to swelling in the presence of solvents [71]. These properties render silane-coated substrates as ideal model surfaces to study a wide range of physical, chemical and biological phenomena such as adhesion, adsorption, friction or nanofluidics of thin liquid films [72-74].

(3-Aminopropyl)triethoxysilane (APTES) is one of the most widely used organosilane agents for the preparation of amine terminated films. Fig. 8 summarizes the silanization process for obtaining APTES films on Si. The presence of -NH₂ head groups on the surface has a major importance for e.g., biological applications allowing attachment of NPs functionalized with protein or other biomolecules [75]. An APTES monolayer results in a mildly hydrophilic surface (contact angle for water, 51°).

Octadecyl trichlorosilane (OTS) is another widely used CH₃-terminated alkyl silane with a chain length of 18 carbon atoms in the backbone. On appropriate surfaces, the OTS molecules self-assemble into crystalline or near crystalline order (depending on temperature) with a hydrophobic head group, Fig. 9. Such coatings are used in applications including, biosensors [76], water resistant coatings [61] and anti-corrosive coatings [77]. The resulting surface of a polished Si substrate after OTS deposition is highly hydrophobic (contact angle for water, 108°).
Fig. 9. The formation of OTS monolayers resulting from a condensation reaction between a hydroxylated Si surface and the hydrolyzed chlorine atoms of OTS. These molecules bind to the surface via hydrogen bonding and finally form \( \text{Si(Silane)} - \text{O} - \text{Si(Substrate)} \) bonds and \( \text{Si(Silane)} - \text{O} - \text{Si(Silane)} \) cross linking covalent bonds [78].

Uniform and high-quality organosilane SAMs of APTES and OTS on Si substrates were obtained using vapor deposition. The wafer was first rinsed with acetone and distilled water, followed by a treatment with Piranha solution at 80° C for 1 hour. The wafer was then washed with distilled water, dried under nitrogen and exposed to UV-Ozone for 30 minutes. Then, 3 ml of silane solution was filled in a beaker and the wafer was exposed to the vapor (upside-down). The setup was placed in a vacuum oven (evacuated to 100 torr) for 16 hours. Thereafter, the wafer was annealed at 110° C at 100 torr for 30 minutes. Finally, the wafer was rinsed sequentially with acetone, isopropanol, water, and dried under nitrogen.

Magnetic substrate with perpendicular anisotropy

Ferrimagnetic amorphous \( \text{Tb}_{15}\text{Co}_{85} \) films can be sputtered onto Si substrates and function as magnetic templates. The films have a strong perpendicular magnetic anisotropy [38] and may generate a worm-like domain pattern [79], see Fig. 10. In the out-of-plane direction, the hysteresis loop is square with a large remanence, \( M_r \), whereas in the in-plane direction the loop is smoothly varying with a small remanence. TbCo films are used for magnetic data storage [80], spin-valve technologies [81] and optical magnetic switching [82].
Amorphous Tb$_{15}$Co$_{85}$ film (∼40 nm thick) were grown using DC magnetron sputtering onto a Si crystal (50×50×10 mm) in zero magnetic field. The samples were prepared in an ultra-high vacuum chamber at room temperature under a pressure of 1×10$^{-3}$ Torr and using 99.99 % pure Ar as sputtering gas. The Si substrates were pre-heated at the base pressure to 650 °C for 20 min and then cooled down to room-temperature before deposition. A 10 nm layer of amorphous Al$_{70}$Zr$_{30}$ was deposited as buffer layer as well as as capping layer (∼5 nm thick) to prevent oxidation [79]. The resulting layer sequence was Al$_{70}$Zr$_{30}$/Tb$_{15}$Co$_{85}$/Al$_{70}$Zr$_{30}$/SiO$_2$/Si. The magnetic template was characterized by NR measurement performed on the reflectometer MAGIK at NCNR. The resulting layer thicknesses, roughnesses and densities are summarised in Table 2.

**Table 2:** Magnetic template Al$_{70}$Zr$_{30}$/Tb$_{15}$Co$_{85}$/Al$_{70}$Zr$_{30}$ sputter grown on a Si wafer. Tabulated are fit results of NR data measured against D$_2$O.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness [nm]</th>
<th>Roughness [nm]</th>
<th>SLD [$10^{-4}$nm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{70}$Zr$</em>{30}$</td>
<td>4.96(35)</td>
<td>2.00(16)</td>
<td>1.78(23)</td>
</tr>
<tr>
<td>Tb$<em>{15}$Co$</em>{85}$</td>
<td>40.47(46)</td>
<td>2.83(41)</td>
<td>2.94(13)</td>
</tr>
<tr>
<td>Al$<em>{70}$Zr$</em>{30}$</td>
<td>11.51(27)</td>
<td>1.71(64)</td>
<td>2.44(8)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.87</td>
<td>0.62(5)</td>
<td>3.8</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
<td>2.07</td>
</tr>
</tbody>
</table>
4. Neutron scattering techniques for investigating colloidal particle assembly at silicon interfaces

The neutron together with the proton forms the elementary building blocks of nuclei. It holds one up- and two down-quarks and has no net charge. Some of its intrinsic properties are listed in Table 3.

Table 3: Neutron properties [83, 84]. $\hbar$ is related to the Planck’s constant $h = 2\pi\hbar$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass, $m_n$</td>
<td>$1.675 \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>Energy, $E$ (meV)</td>
<td>$81.81/\lambda$ (Å$^2$)</td>
</tr>
<tr>
<td>Spin, $s$</td>
<td>$-\hbar/2$</td>
</tr>
<tr>
<td>Magnetic moment, $\mu$</td>
<td>$-9.649 \times 10^{-27}$ JT$^{-1}$</td>
</tr>
<tr>
<td>Electric charge, $Q$</td>
<td>0</td>
</tr>
</tbody>
</table>

Neutrons have several unique properties making them a powerful tool to probe nanostructures in complex sample environments:
- their wavelength (~0.1 nm - 1 nm) is comparable to that of inter-atomic distances in materials thus enables structural studies.
- they are nondestructive to the samples.
- they are highly penetrating into some materials such as silicon and aluminum, with negligible interactions and allow to probe buried interfaces.
- they interact with the nucleus, enable the investigation of light elements and are isotope sensitive.
- their spin is directly sensitive to the magnetic induction in a material.
4.1. Neutron reflectivity

Neutron reflection is a neutron scattering technique that probes structures at and across interfaces by measuring the reflected neutron intensities as a function of neutron wavelength and scattering angle with respect to the sample surface. Reflectivity (R) is the ratio of the intensity reflected from an interface and that of the incoming beam impinging on an interface. The reflected intensity provides information about the density, thickness of a layer as well as the roughness across interfaces.

Fig. 11 presents the scattering geometry for a reflectivity experiment. An incoming neutron beam impinges on an interface under a small incident angle \( \theta_i \) and is reflected at an angle \( \theta_f \). Above the angle of total external reflection, part of the intensity is transmitted (refracted) beyond the interface under an angle \( \theta_r \).

Specular reflection is defined when the angle of incidence is equal to the angle of reflection (\( \theta_i = \theta_f \)) and is used to reconstruct laterally averaged compositional depth profiles along the normal to the surface. In analogy to classical optics, the wave function of the reflected and refracted waves can be calculated by introducing an index of refraction \( n \):

\[
n = \frac{k_t}{k_i} = \frac{\cos \theta_i}{\cos \theta_t}
\]

(4.1)

here, \( k_i = 2\pi/\lambda \) symbolizes the wave vector of the incident neutron beam in air and \( k_t \) the wave vector inside the material. \( \lambda \) is the wavelength of the neutrons. By introducing the scattering potential for neutrons, the index of refraction can be written as

\[
n = \sqrt{1 - \frac{\lambda^2}{\pi N b}} = \sqrt{1 - \frac{\lambda^2}{\pi \rho}}
\]

(4.2)
with \( N \) being the isotope number density and \( b \) the coherent nuclear scattering length. The latter characterizes the interaction between the nucleus and the neutron. It varies randomly across the periodic table and is different for different isotopes of an element [85]. The quantity \( \rho \) is the scattering length density (SLD) of the material and is defined as the product of the number density and the scattering length. The SLD values relevant for this dissertation are tabulated in Table 4.

### Table 4: SLD values of materials relevant for this thesis [86].

<table>
<thead>
<tr>
<th>Materials</th>
<th>SLD (10^{-4}\text{nm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(_2)O</td>
<td>6.33</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-0.56</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>6.91</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>0.57</td>
</tr>
<tr>
<td>Polypropylene oxide</td>
<td>0.35</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>4.18</td>
</tr>
<tr>
<td>APTES</td>
<td>0.1</td>
</tr>
<tr>
<td>NHS</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Light and heavy water have very different SLDs allowing good contrast between particular components in a sample. In the case of magnetic NPs, the SLD of pure H\(_2\)O is typically close to that of the particles shell material while that of pure D\(_2\)O is close to magnetite (the magnetic core). Moreover, the SLD of D\(_2\)O is large resulting in high reflectivity. For the studies presented in this thesis, a high fraction of D\(_2\)O in the solvent was chosen to highlight the particle shells and have a high reflectivity signal [87].

Equation 4.1 does not have a solution as long as \( \sin \theta > n \) and a critical angle for total external reflection (\( \cos \theta_c = n \)) can be defined. For incident angles smaller than the critical angle \( \theta_c \), all the intensity is total external reflected and only an evanescent wave penetrates into the first few nm beyond the interface. Since typically the interaction potential is very small, the refractive index is very close to 1 and the square root in equation 4.2 and the cosine in equation 4.1 can be Taylor expanded. As a result, \( \theta_c \) can be rewritten as [88]:

\[
\theta_c \approx \lambda \sqrt{\frac{N b}{\pi}}. \quad (4.3)
\]
Equation 4.3 contains the incident beam angle as well as the wavelength, which are both parameters that can be chosen by the setting of the instrument. In order to generalize the equation, the vector of momentum transfer is defined as the difference between final and initial neutron wavevectors [89]:

\[ Q_z = \left| \vec{k}_f - \vec{k}_i \right| = \frac{4\pi}{\lambda} \sin \theta. \]  

(4.4)

The critical momentum transfer can be obtained by combining equations 4.3 and 4.4:

\[ Q_c = \frac{4\pi}{\lambda} \sin \theta_c \approx 4\sqrt{\pi N b}. \]  

(4.5)

For momentum transfers larger than the critical momentum transfer \( Q_z \), the reflectivity is described by the Fresnel equation:

\[ R = \left| \frac{\sin \theta - n \sin \theta_i}{\sin \theta + n \sin \theta_i} \right|. \]  

(4.6)

For larger \( Q_z \), the reflectivity drops proportional to \( Q^{-4} \). An example is shown in Fig. 12 (a, dashed) where, the intensity for a Si wafer (with no roughness) is totally externally reflected up to critical momentum transfer \( Q_c = 0.1 \) nm\(^{-1}\) and then drops steeply proportional to \( Q^{-4} \) at larger \( Q \) values. The SLD profile is shown as well in the right panel of the illustration.

Rough interfaces result in a smearing of the step in the SLD. For the case of Gaussian roughness or interdiffusion (both indistinct for specular reflectivity measurements), the SLD profile across an interface can be described by an error function and the reflectivity can be calculated analytically. The final result is an exponential damping:

\[ R(Q_z) = R_F(Q_z) e^{-Q_z^2 \rho^2} \]  

(4.7)

where, \( R_F \) is the Fresnel reflectivity from a flat interface and \( \rho \) is the roughness parameter or width of the error function. The damping of the reflected intensity in equation 4.7 is similar to the Debye-Waller factor in ordinary diffraction [90, 91]. Fig. 12(a, solid) depicts the reflectivity for a silicon wafer with a Gaussian roughness of 1 nm and the SLD profile is reproduced in the right panel.
Equation (4.7) gives the reflected intensity from the surface of an infinitely thick layer. The reflectivity for a multilayer structure can be calculated by using Parrat’s formalism [92, 93]. The specular reflectivity from a multilayer structure (stratified medium of known thickness and density) is obtained by the reflectivity of each interface using the Fresnel relation (equation 4.6) recursively for all interfaces. The reflected waves from the interfaces interfere with each other and maxima in intensity can be calculated by Bragg’s law:

\[ n\lambda = 2d_f \sin \theta_{i/f}, \]  \hspace{1cm} (4.8)

with \( n \) being an integer and \( d_f \) the thickness of the film. Introducing the momentum transfer, the difference between minima and maxima can be calculated from:

\[ \Delta Q_z = \frac{2\pi}{a_f}, \]  \hspace{1cm} (4.9)

for \( Q_z \) values much larger than the critical momentum transfer. As an example, Fig. 12(b) represents the reflectivity from an oxidized silicon wafer with an oxide layer of 25 nm thickness and no roughness. The corresponding SLD profile is shown in the right panel.
4.2. Off-specular scattering

For off-specular scattering, the incident angle ($\theta_i$) and the reflected beam angle ($\theta_r$) are different from each other, see scattering geometry in Fig. 11. As a consequence, the vector of momentum transfer $Q$ has a component in the plane of the interface ($Q_x$), and off-specular scattering provides information about both in- and out-of-plane correlations [94].

Fig. 13 shows a typical detector image collected for a sample with strong off-specular scattering. The data was taken on the instrument Platypus at the Australian nuclear science and technology organization (ANSTO, Lucas Heights, Australia). The sample was PF127 (18.5 wt.% solution in D$_2$O) and measured against a Si substrate. At this concentration the PF127 forms micelles and they assemble in a fcc crystalline phase [95, 96]. The intensity is plotted as color map versus the neutron wavelength and exit angle $\theta_r$. The specularly reflected intensity is indicated by the white horizontal line. The (111) reflection of the fcc structure shows up on the specular line for a defined wavelength and exit angle on the specular line, corresponding to a momentum transfer along the surface normal of $Q_z = 0.37$ nm$^{-1}$ (reflectivity profiles shown in Fig. 17). The specular peak is accompanied by off-specular scattering, visible as streak in the data, related to the size of the micellar crystallites in the plane of the solid boundary [97].

Fig. 13. Intensity collected at the detector of Platypus and plotted versus exit beam angles and neutron wavelength. The line of specular intensity as well as the (111) reflection and region for off-specular scattering of a fcc structure are indicated.

Fig. 14 shows the rocking scan taken for the first-order specular (111) reflection at $Q_z = 0.37$ nm$^{-1}$ (wavelength 0.5 nm and scattering angle 1.66°), for a
PF127 sample measured at the Si wafer (paper I). The rocking curve consists of two components. In Born approximation with a cutoff length [98], the in-plane pair correlation function is represented as the combination of two parts

\[ C(R) = \langle \rho(O)\rho(R) \rangle - \langle \rho(O) \rangle^2 \]  

(4.10)

where, \( R \) symbolizes the in-plane distance, \( C \) is the height–height correlation function, and \( \rho \) is the scattering length density. The scattering function separates into two parts as well

\[ S_{tot}(Q) = \langle \rho(O) \rangle^2 \int e^{iQR} d^3R + \int C(R)e^{iQR} d^3R. \]  

(4.11)

The scattering function becomes the sum of specular reflection (first summand) and the off-specular scattering (second summand), represented by the areas marked in red and blue, respectively, in Fig. 14. The specular reflection reveals the depth profile whereas, the off-specular scattering reflects the structural correlations resulting from scattering length density fluctuations parallel to the interface on length scales smaller than the coherence length of the beam, which are typically on a length scale in the micrometer range [97, 99].

![Fig. 14. Rocking curve as well as a fit for the (111) Bragg reflection obtained with PF127 sample against hydrophobic Si. The red region (narrow component) represents the specular reflection whereas, the blue region (broad component) represents the off-specular scattering.](image-url)
5. Scattering experiments and data analysis

The primary technique used in the present work to explore the structure of the interfacial layer at the solid-ferrofluid interface was neutron reflectivity. This chapter describes the liquid cell used during the neutron scattering measurements, the experiment details as well as the models used for the reflectivity data fitting.

5.1. Liquid cell for neutron reflectivity

For the NR experiments, a solid-liquid cell with a loading capacity of 2.5 ml was designed utilizing reference [100]. The wet cell comprises of a 2 mm thick polytetrafluoroethylene (PTFE) gasket (with injection and outlet ports) used for containing and sealing the liquid sample between the silicon crystal (50×50×10 mm) and the polycarbonate base. The crystal and the base plate were clamped together with an aluminum frame that has channels for circulating water (or ethylene glycol), allowing control of the sample temperature. The cell was further supported on a frame for mounting on the neutron instrument. Fig. 15 shows a sketch of the solid-liquid cell.

![Sketch of the solid-liquid cell](image)

**Fig. 15.** Sketch of the solid-liquid cell with cutaway view of the holder for the substrate, liquid and gasket. The figure is adapted from paper I. The scattering geometry is shown on the left-hand side.
5.2. Reflectivity experiments

Polarized neutron reflectivity (PNR) measurements in vertical sample geometry (to avoid sedimentation) determining the assembly as well as the ordering of magnetic NPs on an APTES coated Si substrate under an in-plane field applied using an electromagnet and on a magnetic template (TbCo) without an external field, were performed on the reflectometer MAGIK at the NCNR with a neutron wavelength of 5.0 Å [101]. During the measurements, the beam footprint on the samples was fixed at 25 mm. For selecting the spin state of the incident neutron beam either parallel or antiparallel to the applied field at the sample position, an Al-coil spin flipper and a Fe/Si supermirror were used. The measurements were conducted with the combined efficiency of the polarizers and the spin flippers being larger than 97 %. The raw data were corrected for polarization efficiency, beam footprint and background using the Reductus software package [102]. Note, since no magnetic signal was detected the polarized data have been combined to improve the statistics and polarized neutron reflectometry is not discussed further in this thesis.

Unpolarized NR measurements in vertical sample geometry determining, the influence of addition of small quantity of F127@Fe3O4 NPs on the crystallization behavior of PF127 on various chemically terminated surfaces and the assembly of magnetic NPs on functionalized Si substrates (Piranha treated, APTES & OTS coated) under an out-plane field, were performed on the instruments MAGIK (NCNR, NIST) and MARIA at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching (Germany) [103], respectively.

The unpolarized NR measurements on MAGIK were carried out with a neutron wavelength of 5.0 Å. The sample (F127@Fe3O4 + PF127) was subjected to an in-plane magnetic field of 120 mT applied using two neodymium magnets (50 × 50 × 25 mm³) mounted at the top and bottom of the liquid cell. Temperature was controlled to a precision of ±1 °C by circulating ethylene glycol through the solid-liquid cell frame. Specular reflectivities for the sample measured against Piranha treated and OTS coated substrates were nearly identical except for the intensities of the (111) Bragg reflections, see reflectivities in Fig. 17. Rocking scans were measured for the (111) reflections. For the measurements performed on MARIA which operates using a monochromatic beam and instrument resolution determined primarily by its 10 % wavelength spread, the reflectivity data were collected with two different wavelengths having a small overlap region. Reflectivity data for $Q < 0.042 \text{ Å}^{-1}$ were collected with $\lambda = 10 \text{ Å}$ and in the range $0.035 \text{ Å}^{-1} < Q < 0.2 \text{ Å}^{-1}$ with $\lambda = 5 \text{ Å}$. A magnetic field perpendicular to the Si surface was applied using neodymium magnets.

The reflectivity datasets were background corrected using the software package available at the instrument and fitted with the Parratt formalism implemented in the NCNR software package Refl1D [104] utilizing the super-
iterative algorithm [105]. For each data set, the optimal number of fitting parameters (and thus the optimal number of layers) were determined using the Bayesian information criteria (BIC); 
\[ \text{BIC} = (n - \nu) \chi^2 + \nu \ln(n), \]
where \( n \) is the total number of data points for the measurement, \( \nu \) is the total number of fitting parameters, and \( \chi^2 \) represents the reduced \( \chi^2 \) statistic of the fit, as detailed in Ref. [106].

### 5.3. Layer model for reflectivity data fitting

The formation of ordered NP structures in FFs close to Si substrates was followed by fitting model layer structures to the experimental reflectivity curves. Two models (M1 and M2) are considered, see Fig. 16(a, b). Model M1 (employed for samples FF15 and FF25) divides the first wetting layer (#1) of particles into three sub-layers. The first sublayer (#1a) in contact with the substrate consists of mainly shell material. The second sub-layer (#1b) contains the magnetite cores as well as shell material and D$_2$O/H$_2$O. Finally, the third layer (#1c) is composed of only shell material and water. For M2 (employed for sample FF5), the first wetting layer (#1) at the silicon substrate is not divided into sublayers. This is justified by the volume fraction of core material in sample FF5, which is less than one percent (see Table 1) and therefore, the sub-layers cannot be resolved. Starting from the second wetting layer of particles (#2) both models are identical and no sublayers are considered. For the assembly of the NP on the magnetic substrates always M2 is employed, since the in-plane disorder is larger in this case.

![Fig. 16.](image)

**Fig. 16.** (a-b) Models for ordering of hard-sphere core/shell particles in a hexagonal close-packed structure with and without sublayers. (c, top-view) Model schematics for the arrangement of core/shell particles in a hexagonally defined (close-packed) arrangement. The figure is reproduced from paper III.
To characterize the packing density, a criterion is defined for close-packed (cp) layering by calculations of the SLD assuming fractional packing. Fig. 16(c, top) visualizes the structure of a close-packed layer of spherical particles with six-fold symmetry. Assuming this structure and utilizing the core/shell diameters determined from SANS along with the bulk SLD values of the FF components as extracted from the fits, the SLD of a dense layer can be calculated for different water concentrations in interstitial voids. For the slabs having thickness (c) larger than the lattice parameter \( d_{c+s} \), the SLD values for an ideal close-packed monolayer of NPs are calculated by considering the difference in thickness being filled by the shell material arising from unbound ligands. Alternatively, swelling of the shell material of the NP would also result in the increase in the slab thickness.

The hexagonal unit cell (uc) has a lattice parameter equal to the core/shell diameter \( d_{c+s} \). The volume of this unit cell is

\[
V_{uc} = \frac{\sqrt{3}}{2} (d_{c+s})^2 c \tag{5.1}
\]

with \( c \) being the layer thickness, irrespective of whether M1 or M2 is used. The volume of the magnetite core is given by

\[
V_c = \frac{\pi}{6} d_c^3 \tag{5.2}
\]

and that of the shell material is obtained by

\[
V_s = \frac{\pi}{6} (d_{c+s}^3 - d_c^3). \tag{5.3}
\]

From the respective volume fractions the concentrations of core and shell materials in each layer can be calculated:

\[
C_{cp}^c = \frac{\pi}{3\sqrt{3}} \frac{d_c^2}{(d_{c+s})^2 c}, \tag{5.4}
\]

\[
C_{cp}^s = \frac{\pi}{3\sqrt{3}} \frac{(d_{c+s}^2 - d_c^2)}{(d_{c+s})^2 c}. \tag{5.5}
\]

Close-packed layers of NPs are identified if the SLD of the respective layer lies between the SLD values calculated assuming shell material or water in the interstitial voids. The two scenarios provide an upper and lower limit. Layers with a SLD outside this range are called loose packed. The regions for close-packed layers are indicated by the gray areas in the SLD profiles in the results section.
6. Assembly of magnetic nano-particles at solid substrates

The first section of this chapter describes the influence of addition of a small quantity of magnetic micelles on the crystallization properties of PF127 at the solid-liquid interface. After this, the self-assembly of magnetic colloidal particles at the interface of solid substrates with different coatings and under in-plane and out-of-plane magnetic field is described.

6.1. Tuning of micellar self-assembly with magnetic particles

The neutron reflectivities for a PF127 solution (18.5 % in D₂O) at 27 °C against hydrophilic and hydrophobic Si substrates are shown in Fig. 17. They are almost identical with the difference only in the intensities of the first and second-order Bragg reflections corresponding to the (111) and (222) reflection in a fcc structure [107, 108].

![Fig. 17. NR profiles for the 18.5 % D₂O solution of PF127 measured in the crystalline phase against hydrophobic (OTS coated) and hydrophilic (Piranha treated) substrates.](image)
The intensity of the (111) reflection is larger for the PF127 sample against an OTS coated substrate indicating, that the layering of the micelles is more pronounced at the hydrophobic interfaces [109]. Rocking scans were measured for the (111) reflection. One single Gaussian line with fixed position, width (resolution-limited), and background was fitted to the narrow component (fits shown in paper I). The broad component was fitted by a Gaussian with a variable width. The results are tabulated in Table 5.

Table 5: Intensities of the narrow and the diffuse components for PF127 against hydrophobic and hydrophilic surfaces, along with FWHM values for the diffuse components.

<table>
<thead>
<tr>
<th></th>
<th>Specular (10^{-2})</th>
<th>Off-specular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity (10^{-2})</td>
<td>FWHM (10^{-4} nm^{-1})</td>
</tr>
<tr>
<td>F127 against hydrophobic surface</td>
<td>6.91(119)</td>
<td>2.20(20)</td>
</tr>
<tr>
<td>F127 against hydrophilic surface</td>
<td>2.21(23)</td>
<td>0.34(25)</td>
</tr>
</tbody>
</table>

For small quantities of magnetic micelles (hydrodynamic diameters, 36 and 71 nm) added to the Pluronic solutions (volume ratio PF127:F127@Fe_{3}O_{4} \approx 23:1, represented as samples S1 and S2, respectively), a significantly larger specular intensity is measured for S1 against a hydrophobic surface as compared to a hydrophilic one (see Table 6, without field column). This is consistent with the findings of the samples without magnetic NPs [110].
Table 6: Specular and diffuse intensities (along with FWHM values) against hydrophobic (for S1 and S2) and hydrophilic surfaces (for S1) under applied field (120 mT) and no field.

<table>
<thead>
<tr>
<th></th>
<th>without field</th>
<th>with field (120 mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specular</td>
<td>Off-specular</td>
</tr>
<tr>
<td></td>
<td>(10⁻²)</td>
<td>(10⁻²)</td>
</tr>
<tr>
<td></td>
<td>FWHM (10⁻⁴ nm⁻¹)</td>
<td></td>
</tr>
<tr>
<td>S1 against hydrophobic surface</td>
<td>4.71 (75)</td>
<td>absent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1 against hydrophilic surface</td>
<td>1.85 (10)</td>
<td>0.31 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.64 (40)</td>
</tr>
<tr>
<td>S2 against hydrophobic surface</td>
<td>1.38 (35)</td>
<td>absent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The magnetic micelles with their hydrodynamic diameter (36 nm) are larger than the lattice parameter (28.5 nm) and the dimension of the interstitial cavities (41.4% and 22.5% of the size of the micelles for the octahedral and the tetrahedral sites, respectively) for an fcc crystal. They push the smaller non-magnetic micelles resulting in a significant interdigitation between the segments of the nearby coronas and the formation of defects. With the size of the magnetic micelles in sample S2 even larger, they change the lateral correlations further and the structure becomes richer in defects.

For the PF127 + F127@Fe₃O₄ samples, a strong influence on the (111) reflection is seen after the application of a magnetic field of 120 mT (see Table 6, with field column). The amplitudes of the narrow components become predominant, denoting an improved layering under a magnetic field. The maximum specular intensity is nearly similar for both the surfaces. This is explained by the motion of the magnetic micelles in the in-plane magnetic field past the non-magnetic micelles. The micro-shear effect results in improved crystallinity similar to macroscopic shear [110] and the influence of the interface becomes negligible. Also, the samples show higher diffusely scattered intensity, indicating that the size of the crystallites grew together with the formation of better layering.

6.2. Self-assembly of magnetic particles at modified silicon substrates

In this section, the formation of the wetting layer is investigated in more detail by studying solid substrates with different coatings. The self-assembly process
goes in two steps: First, a wetting/seed layer, resulting from the affinity of the NPs shells and the substrate coating, is formed. Second, the long range dipolar magnetic interaction (as well as the stray fields from the substrate if it is magnetic) triggers the assembly of further layers.

NR data along with the best fits and the corresponding SLD profiles are shown in Fig. 18 for sample FF25 in contact with different treated silicon substrates. The particles do not self-assemble onto the surface coated with OTS. For the three other coatings viz., Piranha, APTES and TbCo, self-assembly is found. The NPs are loosely packed within a single monolayer assembled at the Piranha treated substrate. In comparison, a closely packed wetting layer followed by a second loosely packed layer is obtained on the APTES coated substrate. Similar to this assembly of particles on APTES coated surface, two-particle layers are formed at the magnetic substrate both of which are close-packed. Interestingly, this situation does not change after a careful cleaning and rinsing of the magnetic surface and re-measuring it in contact with D$_2$O. The wetting layer is still present, however, with a slightly reduced thickness and increased SLD, which can be explained by the collapse of the shells during the cleaning procedure and rehydration in D$_2$O during the measurement, respectively.
6.3. Self-assembly of magnetic particles with different size

On a TbCo coated silicon substrate, FF25 sample forms two interfacial layers, similar to this, FF15 and FF5 particles also assemble into two particle-layers at the magnetic surface. For FF5, both the layers are loose-packed while for
FF15, a close-packed wetting layer followed by a loose-packed layer is obtained. Similar to FF25, the packing observed in the smaller samples is retained after surface cleaning. The structural configurations are summarized in Table 7. The data for FF5 and FF15 are shown in paper IV.

Table 7. Structural configurations of the model systems describing the three FF samples measured on a magnetic substrate.

<table>
<thead>
<tr>
<th>Layer</th>
<th>FF5</th>
<th>FF5 after cleaning</th>
<th>FF15</th>
<th>FF15 after cleaning</th>
<th>FF25</th>
<th>FF25 after cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>Loose</td>
<td>Loose</td>
<td>Close</td>
<td>Close</td>
<td>Close</td>
<td>Close</td>
</tr>
<tr>
<td>Second</td>
<td>Loose</td>
<td>Loose</td>
<td>Loose</td>
<td>Loose</td>
<td>Close</td>
<td>Close</td>
</tr>
</tbody>
</table>

The assembly of colloidal particles with different sizes was also studied against an APTES coated silicon surface where the first layer formed due to chemisorption of the particles at the surface and the next layer due to magnetic dipolar interactions. NR data, multiplied by $Q_2$, for the samples FF5 and FF25 (5 vol. % solved in D$_2$O/H$_2$O ratios of 0.86/0.14 and 0.78/0.22, respectively) measured against APTES coated Si are shown in Fig. 19 (left panel) and plotted as a function of $Q_z$. Data are taken with the samples in zero magnetic field. The best fit to the data with the corresponding $\chi^2$ (marked), are shown as solid-lines. The corresponding Nb(z) profiles for FF5 and FF25 are displayed in the right panel.
For FF5, the wetting layer (defined in M2) at the APTES interface is a close-packed particle-monolayer consisting of a mixture of shell material (ligands attached to the NPs and in the interstitial regions between the NPs), excess surfactant, core material, and water. No additional NP layers can be differentiated between this slab and the bulk liquid for FF5. For samples FF15 (data shown in paper III) and FF25, a close-packed wetting layer (defined in M1) followed by a loose packed layer is obtained.

6.4. Magnetic particle assembly in an out-of-plane magnetic field

In an earlier study (paper II), the self-assembly of magnetic colloidal particles (size ~25 nm) was studied at an APTES terminated surface. The particular sample includes dimers and trimers. It was found that NPs form a densely packed layer at the substrate surface despite their low volume concentration (0.15 vol.%). Under an in-plane magnetic field of 6 mT, a double NP layer
consisting primarily of tilted dimers is formed above the wetting layer. A further larger in-plane field of 100 mT results in the layer splitting into two distinguishable NP layers. In this section, the influence of an out-of-plane magnetic field on the colloidal magnetic particle assembly at the solid-liquid interface is investigated. It can be expected that an out-of-plane field promotes the self-assembly of particles into layer structures as the particle arrangement into a head to tail configuration is preferred.

All three samples (FF5, FF15 and FF25, 5 vol. % in D$_2$O/H$_2$O and measured at APTES surface) were subjected to a magnetic field of 100 mT applied out-of-plane for two and twelve hours. The self-assembled NP layers are in Table 8. FF5 (0.5 vol. % against APTES) was also measured under 100 mT applied out-of-plane for two and twelve hours. This was followed by 250 mT applied for two hours.

Table 8: Layer structure extracted from model calculations based on the results from SANS and NR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. (vol. %)</th>
<th>Assembled particle-layer</th>
<th>Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0 mT</td>
</tr>
<tr>
<td>FF5</td>
<td>5</td>
<td>First</td>
<td>close</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>-</td>
</tr>
<tr>
<td>FF15</td>
<td>5</td>
<td>First</td>
<td>close</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>loose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Third</td>
<td>-</td>
</tr>
<tr>
<td>FF25</td>
<td>5</td>
<td>First</td>
<td>close</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>loose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Third</td>
<td>-</td>
</tr>
<tr>
<td>FF5</td>
<td>0.5</td>
<td>First</td>
<td>loose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>-</td>
</tr>
</tbody>
</table>

After two hours of field application, additional particles wet the surface for all samples. In sample FF5, a continuous densification of a second particle layer with time is found. In both FF15 and FF25, the initial loose-packed second layers become close-packed after two hours. For sample FF25, even an additional third loose packed layer is reported. Applying the magnetic field for
layers become close-packed after two hours. For sample FF25, even an additional third loose packed layer is reported. Applying the magnetic field for longer times, after twelve hours, results in the densification of this third layer, which becomes close-packed. After this time with 100 mT applied also for sample FF15, a third loose-packed layer is reported. See Fig. 20 for the NR data along with the best fits and the corresponding Nb(z) profiles for the samples FF5 and FF25, under magnetic field of 100 mT applied out-of-plane for two and twelve hours. In diluted FF5 (0.5 vol.%) measured against the APTES coating, a loose-packed wetting layer is found unlike the close-packed layer found with the concentrated sample shown in Fig. 19. However, only a single particle-layer is found with both samples. This shows that there are no large effects of the NP concentration. The particles in the wetting layer couple with the substrate through strong chemical linkages and additional layers form due to magnetic dipolar interactions which increases with particle size. Therefore, particles in diluted FF5 solution do not form a second-particle layer even when a magnetic field of 100 mT is applied out-of-plane for twelve hours. Increasing the field to 250 mT does have an effect on the particle assembly as now the second-particle layer can be observed but is still loose-packed.
Fig. 20. NR ($R Q_z^4$) taken under magnetic field of 100 mT applied out-of-plane for two (red) and twelve (blue) hours, for samples FF5 (left panel) and FF25 (right panel) and plotted versus $Q_z$. The solid lines (black) represent fits to the data. The panels in the center and lower row show the resulting SLD profiles plotted as a function of distance from the Si (100) surface. The grey areas represent the SLD ranges for close packed layers of particles.

From the study of different surface terminations of the silicon substrates presented above, it is clear that only for an appropriate coating the magnetic NPs may assemble. This can be well understood since the particles reach the surface in a statistical manner and only stick to it if short range attractive interactions exist.

Fig. 21 summarizes the formation of the first wetting layer by either, physisorption or chemisorption, panels upper right and bottom left, respectively. Improved wetting properties are achieved by using specific chemical anchors viz., NHS molecules on the NPs and APTES on the substrates. The NPs (activated through EDC-NHS chemistry described in section 2.3) chemically couple with the APTES coated substrates by a strong bonding (-CONH bond), see Fig. 21 (bottom left). Piranha treated hydrophilic substrates present hy-
droxy (-OH) terminations (Fig. 8) to the carboxylic polarities of the NPs, resulting in a hydrogen bond formation between the two. The bond is strong but weaker than the -CONH bond obtained with APTES [111]. The OTS coating is a methyl (CH$_3$)-terminated alkylsilane (Fig. 9). The ligands charge stabilizes the NPs in water and are strongly hydrated (see Fig. 21, upper left panel). As such they can be treated as hydrophilic and show no affinity to the OTS coating, which is strongly hydrophobic.

**Fig. 21.** Magnetic self-assembly of NP at Si substrates with different surface termination. For the case of chemisorption, a dense wetting layer of magnetic particles is formed, which allows the assembly of adjacent layers via the magnetic dipolar interaction.

The particles in sample FF5 are inherently SPM at room temperature. Therefore, for FF5 in contact with APTES, only a loose packed wetting layer at 0.5 vol.% and only one single particle-layer at 5 vol.% (unlike FF5 and FF25 forming two particle-layers at the surface) is observed (Table 8 and Fig. 19). The volume fraction of magnetic core material in these particles is below one percent and even at dense packing the distance between cores is relatively large and no induced moments between NPs can be expected. The NPs in samples FF15 and FF25 are slightly or clearly above the SPM limit for Fe$_3$O$_4$. Therefore, the individual NPs are ferromagnetic and single domain. When adsorbed at the silicon substrates the NP cores come closer to each other and may interact via magnetic dipolar forces. This results in the formation of magnetic domains in the wetting layer. The magnetization in the domains is expected to be in the plane of the substrate and result in an attractive force between adjacent particles. However, at the domain walls, out-of-plane stray fields exist. The stray fields decrease with increasing distance from the substrate and, a force is exerted on the dispersed NPs due to their magnetic dipole moment and the field gradient. As a result, further layers depending on the
magnetization of the NP, may assemble at the interface (see Fig. 19, green curve). The situation changes on the application of an out-of-plane magnetic field. Since, all samples behave collectively SPM, the magnetization of the NP will align with the external field and point out-of-plane (Fig. 21, bottom right). Moreover, only part of the substrate is covered with magnetic cores, since, even in the case of dense packing, in between them either shell material or water is found. In total, this results in field gradients and out-of-plane magnetic fields, which attract NPs from solution. Whenever a NP reaches the wetting layer it gets stabilized above the particle in the first wetting layer to have a head to tail magnetic moment. As a result, we observe additional wetting layers for all three samples developing with time in an out-of-plane magnetic field (Table 8 and Fig. 20). For longer times as well as larger magnetic fields the layering becomes more pronounced.

Clearly and as expected from the discussions of the magnetic moment of the particles, more dense packed layers are formed for the particles of larger size, since they have larger moments and have a larger volume fraction of cores in dense layers. At the same time a lower water content is found in the layers (see paper III and IV for details). Under the application of an out-of-plane field in all samples additional layers assemble and the ones already existing at zero field become denser. This observation continues over at least twelve hours, which is the longest time investigated in this study. After this time for sample FF15 even a third LP layer is observed, which become even CP for sample FF25.

An alternative approach using a ferrimagnetic layer of TbCo deposited on the silicon substrate as the template layer results in a stronger binding of the wetting-layer particles with the solid surface. A schematic for the assembly at the magnetic substrate is shown in Fig. 22. The FF5 particles show loose packing (Table 7), and similar to the measurement at APTES, FF25 particles show most pronounced self-assembly due to their large remanant moment (both the wetting layers as well as the layers in between the wetting layer and the bulk are densely packed). For the three samples, only minute changes in reflectivity are found after a thorough cleaning and rinsing of the substrate, indicating the assembled layers to be very stable. SEM micrographs of the substrates (see paper IV) taken before and after cleaning, indicate that a close or loose packed layer can also be assumed as dense patches with gaps filled with solution in between. The extracted surface coverage was compared to the NR results qualitatively. The results show that particles at the magnetic substrate settle preferentially at the domain walls due to high magnetic flux at the position and, assemble into patchy areas of dense layers. The results sections 6.2 and 6.3. are summarized in paper VIII.
Fig. 22. Magnetic self-assembly of NP at Si substrate coated with a ferrimagnetic film of TbCo possessing perpendicular anisotropy. The particles are influenced by the stray fields from the substrate and assemble at it.
7. Ferro-fluids applied as electrical contacts

Building on the understanding of the interactions in magnetic colloids, this chapter describes the application of percolated structures in magnetic liquids as electrical switches. The first section introduces the concept of effective moments tunable by the magnetic volume susceptibility of the solvent matrix. The second section describes the microbeads, the sample cells and the experimental setups. The next section presents the transmission and switching characteristics of the liquid tuned under applied magnetic and electric fields. At last, the correlation between the transport properties and the self-assembly of beads into percolated structures between two electrodes on the basis of microscopic observations is discussed.

7.1. Concept of effective moments and experimental setup

For a mixture of monodisperse magnetic and non-magnetic beads dispersed in a FF, the interaction between the beads can be described by an effective magnetic susceptibility [28]. Analogous to the Archimedes principle, the microbeads dispersed in a homogeneous medium (here FF) displaces it by their volume and their susceptibility is effectively changed by the susceptibility of the medium. Magnetic beads exhibit a reduced paramagnetic response and non-magnetic beads become effectively magnetic with an effective magnetic moment equal to that of the displaced FF. The effective moment of the diamagnetic particles is \( \vec{m} = -V \chi_{\text{eff}} H \), where \( V \) is the particle volume, \( \chi_{\text{eff}} \) is the effective volume susceptibility of the FF and \( H \) is the applied magnetic field [112].

Cartensen et al. [28] studied the behavior of such magnetic microparticles in a FF and obtained meta-stable structures, e.g. branching chains. Further, they tuned the microparticle interactions by varying the FF susceptibility, leading to the formation of a variety of phases in the binary colloidal system. In this thesis, similar microparticles are investigated but with the difference of an additional 50 nm thick gold coating allowing electrical conductivity via a percolated structure.
The conducting polystyrene beads with a nominal diameter of 10 μm were commercially obtained from MicroParticles as 20 mg/ml stock solutions. Two types of particles were used with the only distinction that one has a ferromagnetic Ni coating layer, while the other one does not, see Fig. 23 (left). Scanning electron microscopy [113] was used to image the beads, see Fig. 23 (middle). The beads are monodisperse with uniform shape and size. The gold shell was verified by Energy Dispersive X-Ray Spectroscopy (EDS) [114], Fig. 23 (right). A homogenous coverage is crucial for good conducting properties of the particles.

![Fig. 23.](image)

Fig. 23. (left) Schematic of the beads used for the electrical contacts. (middle) SEM images of the gold coated PS beads along with the corresponding EDS images (right) demonstrating a full coverage with gold. Images adapted from paper V.

After verification of the particle quality, 10 μl of 40 mg/ml of microbeads (1:1 ratio) were dispersed in a 15 μl of a mineral oil-based FF matrix (FePt alloy NPs, ~40 nm diameter, 1.1 % vol. fraction + gold NPs, 50 nm diameter, 5 mg) with a volume susceptibility of $\chi_F = 0.21$. As a result, the non-magnetic particles obtain an effective magnetic moment as described above and couple anti-ferromagnetic to the magnetic particles of susceptibility $\chi_m = 0.26$. Once prepared, the solutions have been investigated in two sample cells. One is optimized for surface area to switch larger currents (Fig. 24, left panel) while the second allows in-situ optical microscopy (Fig. 24, right panel). The cell optimized for current transmission consists of circular wells (10 mm diameter and 1.5 mm depth) in polypropylene casings. Two copper electrodes (10 mm diameter and 1 mm thick) were coated with 100 nm thick gold layer deposited by thermal evaporation, and placed inside the circular wells and connected to copper wires. For sealing, rubber O-rings are used in grooves of the polypoylene casings, clamped together by metal screws. The sample thickness between the electrodes is 1 mm. For the cell for in-situ microscopy shown in Fig. 24 (right panel), 0.5 mm deep grooves were grinded in a transparent polypropylene disk and gold electrodes (length 10 mm and diameter 1 mm) were placed at a distance of 1 mm.
Fig. 24. Liquid cells for (left panel) measuring electrical conductivity through a magnetic fluid and (right panel) for observing the micro-beads with transmission optical microscopy.

The cells were placed in vertical orientation between two copper coils creating a magnetic field. For fields above 100 mT iron pole-shoes were added. A Hall-probe was used to monitor the magnetic field close to the cells. An electrical potential was applied by a DC source and the current through the liquid was measured by an amperemeter connected in series. The voltage applied across the sample and the current in the coils generating a magnetic field was controlled by a LabView program.

7.2. Current transmission and switching performance

Subjecting the sample to a constant voltage of 5 V followed by magnetic fields between 0 to 420 mT (intervals of 120 mT, 180 mT, 320 mT, and 420 mT) shows that the composite exhibits current transmission dependent on the applied magnetic field and increasing with time, see Fig. 25(a). For the magnetic field interval 0-180 mT, two distinct regimes are observed. The initial raise in current results from the percolation of the particles, while the subsequent slower process is related to the gradual assimilation of particle clusters into the transmission channels connecting the two electrodes. At larger magnetic fields only one exponential time constant is found. This is most likely related to an increasing density of particles between the electrodes.
Fig. 25. (a) Current vs. time characteristics for 10 μl of 40 mg/ml of microbeads (1:1 ratio) dispersed in FePt and gold NPs based oil matrix, plotted as a function of time and magnetic field. Red lines are guides to the eyes. (b) Logarithmic plot of current vs. voltage obtained when the voltage is gradually increased while keeping a constant magnetic field of 420 mT (black curve). The green circle marks the threshold voltage and the red circle marks the maximum current following a voltage drop. Red curve shows the characteristics when the sample is subjected to a high voltage of 51.47 V, however, in the absence of a magnetic field. Data reproduced from paper V.

When the sample is subjected to a constant magnetic field of 420 mT and a voltage is applied gradually, the conductivity is zero for voltages below 4.1 V, see in Fig. 25(b). The current increased rapidly at higher voltages till a threshold voltage ($V_{TH} = 20.2$ V). The conductivity for the sample at 20 V (just below $V_{TH}$) was measured to be 0.81 mS/m. For voltages above 50 V, the composite shows conducting characteristics related to the evaporation of the solvent and a resulting short circuiting.

Fig. 26 shows current measurements for a liquid subjected to an initial condition of 420 mT in-plane field and 5 V voltage, thus, transmitting 100 μA current. Once an out-of-plane magnetic field of 600 mT is applied the current decreases but does not vanish. Only after removing the magnetic in-plane field, an immediate decrease in current to about 13 μA is observed. After further four seconds, the current further reduces to instrument zero.
Fig. 26. From an initial condition of the liquid being under 420 mT in-plane field and 5 V potential, attempts were made to break the contact by disturbing the structure formed by the conducting beads between the two electrodes. (left) Time plot obtained when 600 mT was applied out-of-plane in order to break the contact. (right) Time plot showing current transmission stopping after removing the applied magnetic field.

The transport properties of the liquid sample can be related to the self-assembly of the microbeads. Fig. 27 shows images from optical microscopy reproduced from paper V. As seen in the photograph the formation of chains is seen immediately after the application of a magnetic field. Note, the contact area of the electrodes in the cell used for optical microscopy is smaller than in that used for the conductivity measurements. So, it is well conceivable that some chains connect the electrodes in the conductivity setup explaining the initial and fast raise of the current, visible in Fig. 25 (a). Once an additional electric field is applied a slow increase in the total density of the particles between the electrodes is found. This explains the second time constant visible in Fig. 25 (a), since with increasing particle density the conductivity is expected to raise. The increasing density may be explained by the electrical dipole moment of the conducting beads. Once, an electrical field is applied the particles become electrical dipoles. At the same time at the ends of the chains a large electrical field density is found attracting the electrical dipoles. As a consequence, the chains grow and allow an increasing transmission of current. Once the magnetic field is removed the only interaction keeping the chains together is the electrical dipole interaction and some chains break and the current gets reduced. Note again, the geometry of the optical experiments is very different from the one used for the conductivity measurements and a direct quantitative connection is not possible. However, the results show that measurements of
electrical currents may actually be a good measure of percolation in FF systems and allow to address the dynamics in such systems.

**Fig. 27.** A sequence of CCD-camera images showing bead assembly under magnetic and electric fields. The box in the top right shows the size and the position where the images were taken between the electrodes along with the marked directions of the applied fields (left to right). Dotted lines in between images mark the change of condition, i.e., toggle between the applied fields. (a) Beads under magnetic field of 70 mT. (b-c) Under potential, the beads are attracted towards the electrode on the right. (d) Begin to line-up at the electrode. (e) Branching emerges and percolation starts to appear. (f) Removing magnetic field breaks the chain, viz. percolation and thus the current.
8. Summary and Outlook

The present work shows that the addition of small quantities of large magnetic micelles (hydrodynamic diameter 71.6 nm) to 18.5 wt. % D$_2$O solution of PF127 result in a more distorted crystal resulting from the fact that the magnetic micelles do not fit into the crystal lattice and cause defects. Once a non homogenous magnetic field is applied, the magnetic micelles move along the gradient resulting in a micro-shearing effect which aligns the crystallites in the micellar structure similar to macroscopic shear (paper I).

On an APTES functionalized Si surface, water dispersed magnetic NPs (∼25 nm diameter, 0.15 vol. %) assemble into a close-packed particle wetting layer. An in-plane magnetic field promotes further densification, particle layering and quasi-domain formation in closely packed layers (paper II). An out-of-plane field applied results in a similar structural assembly, however, with dense packing only for the larger particles with larger magnetic moments (paper III). More concentrated solutions (5 vol. %), in general, show more pronounced layering. Increasing the applied magnetic field results in further densification of the wetting layers. Apart from the APTES coating, the self-assembly of magnetic NP was studied at Piranha treated, OTS coated and TbCo film coated interfaces. As expected, the density of the wetting layer becomes larger for stronger particle-coating interactions. At a TbCo film, the three Fe$_3$O$_4$ particle sizes show a similar structural assembly as found against the APTES coating under out-of-plane applied magnetic field. However, the NPs are more firmly attached at the magnetic surface as the wetting layer remains mostly intact after rinsing the substrate (paper IV).

In summary, the physics involved in directed self-assembly, which is an excellent way for designing future metamaterials, is revealed. Specular NR is used to extract information about the layering of colloidal magnetic NPs at solid substrates. The key result is that directed self-assembly resulting from the magnetic dipolar interaction between NPs critically depends on the formation of a first wetting layer at the solid boundary. This first layer is formed for a strong and attractive interaction of either the magnetic moment of the particles themselves with the magnetization of a coating layer, or chemical bonds between a self-assembled monolayer on the substrate and the ligand shell of the particles. In these cases, a dense and flat wetting layer forms, which allows the adsorption of further layers resulting from the magnetic dipolar interaction between the magnetic particles and a well ordered structure.
develops with time. For larger moments of the magnetic particles, the ordering is more pronounced and forms on a shorter time scale.

This knowledge on the interactions in magnetic colloids was utilized to realize a liquid switch by applying a magnetic field to a colloidal dispersion of conducting magnetic and non-magnetic polystyrene beads suspended in an oil-based FF. The resulting percolated structure allows a precise control of current transmission as well as switching. The contact is scalable and can find possible applications in fields like automotive, switchboard and telecommunications. Moreover, such a contact might be capable of offering a lower loss current conduction (for low or medium voltage applications) compared to contemporary mechanical connections and may solve challenges such as oxidation, mechanical wear, contact welding/sticking and contact erosion [115]. The work also demonstrates the application of such a contact as a switch which could potentially replace traditional electromechanical switches [116].

It turns out that the transport of electrical current is very sensitive to the combination of electrical and magnetic fields. Once a magnetic field is applied to a magnetic colloid the particles self-assemble in strings allowing the transmission of current. At the same time, high electrical field densities are present at the end of the strings. This results in an additional attractive force, due to the electrical dipole moments induced in individual particles. As a result, more particles assemble and allow the transmission of larger currents. The two processes are characterized by different time constants connected to self-assembly on short length scales and a longer-range diffusion into the capacitor. The results show that transport measurements may be an excellent complement to optical methods for the study of percolation in colloidal systems.
Svensk sammanfattning

Självmontering är en ekonomisk metod som ger kontrollerbara och enkla mekanismer för att arrangera nano-partiklarna i tredimensionella ordnade strukturer, som visar anmärkningsvärdiga kollektiva egenskaper (skiljer sig från deras isolerade motsvarigheter). Dessa strukturer kan erhållas antingen genom direkt interaktion mellan byggstenarna eller med hjälp av en mall eller ett extern fält.

Nanopartiklar när de sprids i flytande form kolloid. I kolloider kan komponenterna interagera med varandra eller deras medium för att spontant bilda hierarkiska strukturer när systemet utvecklas mot jämvikt. Avstämbarheten för interaktioner mellan de enskilda partiklarna gör självmontering av koloidala partiklar till en attraktiv väg för tillverkning av strukturer med skräddarsydda mekaniska, elektroniska eller magnetiska egenskaper. Smarta, funktionella och stimulerande responsiva syntetiska material kan realiseras med en djupare kunskap om sådana system.

Riktad självmontering kan uppnås genom att exempelvis uppnås genom användning av magnetiska nano-partiklar och kan göras mycket mångsidig genom att använda t.ex. magnetfält. Fältet utlöser ett snabbt, anisotropiskt och reversibelt svar till följd av magnetiska interaktioner och kan resultera i ordnade strukturer såsom linjära eller grenade kedjor samt kluster med avstämbar kristallinitetsgrad. Således blir applikationer som medicinsk bildbehandling, läkemedelsleverans, fotonik, datalagring etc. tillgängliga.

I denna avhandling studeras självmontering av koloidala magnetiska partiklar i organiserade och flerskiktade strukturer. Särskild tonvikt läggs på gränser för fast vätska och svaret på applicerade magnetfält. Små mängder magnetiska miceller i en hybridmagnetisk polymer nanokomposit underlättar kristallisationen av Pluronic F127 miceller löst i vatten i enstaka kristallina strukturer vid gränsytan fast-vätska via en mikroskjuvningseffekt under applicerat magnetfält.

För montering av magnetiska koloidala partiklar vid de fasta substraten stabiliseras specifika funktionella molekyler inte bara partiklar i lösningen utan främjar också deras sammansättning vid ett substrat. Ett exempel i detta sammanhang är N-hydroxisuccinimid som interagerar med (3-aminopropyl) trietoxisilan vid substratet. Som ett resultat av denna kemiska affinitet såddes enhetliga och tätt packade partikelfuktande skikt som sedan inför lagringsprocessen. Som ett alternativ till kemisk bindning inducerar det magnetiska lövfältet i en ferrimagnetisk avsätt vid ett substrat även partikelförsamling med
täta skikt. Tillämpningen av ett externt magnetfält främjar ytterligare förtät-
ning och partikelskiktning. Liknande strukturlagring erhålls med applicering
av magnetfält oavsett orientering, i plan eller längs ytans normala. Partikel-
skikt med tätare packning återfinns emellertid i plan-orienteringen. I allmän-
het är självmontering en relativt långsam process och utvecklas över timmar
och är maximerad, mest ordnad och tät för nanopartiklar som är enstaka do-
män och har ett stort återstående ögonblick och minskad termisk rörlighet.

Ur applikationsperspektiv kan ett magnetfält applicerat på en kolloidal dis-
persion av ledande magnetiska och icke-magnetiska polstyrenmikrokulor
suspenderade i en oljebaserad ferrofluid leda till perkolerade strukturer. Detta
möjliggör strömöverföring och växling. En fungerande kontakt för möjliga
tillämpningar inom fordonss-, växel- och telekommunikation demonstreras.
My biggest and heart-felt thanks goes to Max. Thanks for accepting me under your guidance and allowing me to be myself. These past years has been a part of an exciting journey all along mostly because I shared it with you. Thanks for always supporting me when times were tough, for always listening when I was complaining, and most of all thanks for always finding pragmatic and reasonable solutions to all my queries.

In Indian culture, knowledge is considered one of the means/virtues to achieve Moksha. It is said in ancient scriptures that if one encounters both God & Guru simultaneously, then the person should always greet the Guru first, since without him, how would he be able to recognize (known) God. Understanding the essence behind this analogy, I truly feel that through you, I really have gained a lot! You have been an amazing supervisor, a fun partner during experiments, an inspiring leader, a resourceful consultant, a wise counsellor (at time a magical therapist) and most of all a wonderful friend whom I shall cherish throughout my life. The list of adjectives to describe the value and respect you command from me is endless.

Vassilios you always stood by me and irradiated calmness, thanks for your patience and always being so positive and encouraging. Thanks for pushing me and making me do more than I thought I was able to. Without your guidance, support and motivation, I would not have been able to achieve this task. Also, now that I can express it, I would like to accept that I am a bit jealous of the vast knowledge & intellect you possess. Sometimes, I wonder whether there is anything you do not know about or can’t possibly have a conversation about? In short, I would go to war with you and Max by my side.

Julie thanks for the immensely helpful scientific discussions and your willingness to explain things. You showed an unwavering interest and engagement into my work. Thanks for calmly explaining the most difficult concepts and facts precisely and with extreme calmness. You found energy to teach me even on weekends. I really feel a deep gratitude for your guidance and support.

Katharina I would like to thank you the most sincerely for your enthusiasm and support during this work. In the very beginning itself you told me that you enjoy working with me. I would like to express that it is me who enjoys greater. Experiments as well as analysis had been fun with your presence. I respect your energy and willingness to complete tasks at hand. It is extremely motivating as well as inspiring. You have not only been a great collaborator but also a great mentor to me. You were calm and optimistic during failed
measurements even when I was being nervous. It is fun to have long discussions with you regarding all domains- life, friends, travel, marriage etc. It was also fun to explore new cities with you and we shall always find the nicest restaurants.

Next, I would like to thank Björgvin for explaining all the possibilities I had during my PhD. Discussions with you had been inspiring. Thanks for pushing me and making me do more than I thought I was able to. Without your guidance, support and motivation, I would not have been able to achieve this task. You showed patience with me while being positive and encouraging. I shall always remember and practice the idea of Occam’s razor you shared with me. Honestly, it has been a great problem-solving principle for me since. Last, I would like to thank you for sharing your valuable insights. Your guidance and help have been indispensable.

My collaborators, Alexei, Alexandros, Joe, Brian, Philip, Andrew, Stephen, Paul and Kathryn. Anton, I would definitely enjoy to drive Tesla with you from France till Singapore.

All the seniors in the group, Adrian, Gabriella, Bengt Petra, Gunnar, Erik. Also, to all the rest of my fellow PhDs: Henry, Sotiris, Shirin, Hauke, Ioan, Tobias, Lennard, Andreas, Emil, Erik. Thankyou Sebastian, for helping me with the TbCo samples, thankyou Hauke for helping me with magnetic colloids and Björn for helping with the MFM images.

Last and most importantly to my Family for always being there for me no matter what. Natasha you are my lady luck. I cherish as well as respect you and I shall keep my promises, Always & Forever! Thankyou for being with me and loving me. You are a wonderful soul and my greatest treasure. Without your support this would not have been possible. Though Aarna made it extremely difficult for me but you helped me sail through. I love you & Aarna the most. This one is for you.
References


Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 1940

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)