# Trapping Ferrofluid Patterns: Insights into Hierarchies of Order from Self-Organization of Magnetic Nanoparticles

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### Abstract

This thesis is concerned with the nanoscale to macroscale origins of pattern formation in selforganizing systems called ferrofluids. In our studies, ferrofluids comprise superparamagnetic magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles suspended in a non-magnetic fluid. When exposed to a magnetic field, the fluid undergoes symmetry-breaking transitions to form extraordinary patterns and structures over multiple length scales. Pattern formation is a manifestation of the phenomenon of self-organization. Strictly speaking, a self-organized system can sustain order only in an out-ofequilibrium state sustained by the input or exchange of energy and/or matter from the thermodynamic system with which it is in contact. In the case of ferrofluids, their patterns collapse when the magnetic field is removed. This thesis describes our efforts to trap these self-organized structures and thus to provide new insight into the morphogenesis of the patterns.

We first introduce ferrofluid pattern formation and self-organization. We then show that the patterns in ferrofluids can be "trapped" as kinetically stable structures assembled from oleic acid (OA) coated magnetite nanoparticles by formulating the ferrofluid as an evaporating medium. We examine the impact of the inhomogeneous magnetic field, nanoparticle concentration, evaporation rate, solvent type and substrate. We show that excess OA ligand, in concert with a complex ferrohydrodynamic response, directs changes in the macroscopic patterns from order to disorder, and transitions from hexagonal to labyrinthine patterns. A crosslinking polymer is introduced as a reaction diffusion system where the exchange of matter in the presence of the applied field induces a new type of morphogenesis. We observe previously unreported hierarchies of order spanning nanometers to millimeters in these structures. Finally, we probe the magnetic properties of the

trapped structures by ferromagnetic resonance and magnetometry. The self-organized structures of interacting spherical, cubic and polydisperse magnetic nanoparticles exhibit emergent properties from their non-interacting counterparts.

In conclusion, this thesis probes the paradigm of pattern formation in ferrofluids into new aspects of morphogenesis enabled by the method of trapping self-organizing magnetite nanoparticles to make hierarchical structures. The technique has wide scope in terms of chemical and physical modifications to broaden inquiry into the fundamentals of self-organization and perhaps to create downstream applications of the self-organized structures that might exhibit emergent properties.

### Résumé

Cette thèse s'intéresse aux origines nanométriques à macroscopiques de la formation de motifs dans des systèmes auto-organisateurs appelés ferrofluides. Dans nos études, les ferrofluides comprennent des nanoparticules de magnétite superparamagnétique (Fe<sub>3</sub>O<sub>4</sub>) en suspension dans un fluide non magnétique. Lorsqu'il est exposé à un champ magnétique, le fluide subit des transitions de rupture de symétrie pour former des motifs et des structures extraordinaires sur plusieurs échelles de longueur. La formation de modèles est une manifestation du phénomène d'auto-organisation. À proprement parler, un système auto-organisé ne peut maintenir l'ordre que dans un état hors d'équilibre soutenu par l'apport ou l'échange d'énergie et / ou de matière provenant du système thermodynamique avec lequel il est en contact. Dans le cas des ferrofluides, ses motifs s'effondrent lorsque le champ magnétique est supprimé. Cette thèse décrit nos efforts pour piéger ces structures auto-organisées et ainsi fournir un nouvel aperçu de la morphogenèse des modèles.

Nous introduisons d'abord la formation de motifs ferrofluides et l'auto-organisation. Nous montrons ensuite que les motifs dans les ferrofluides peuvent être «piégés» sous forme de structures cinétiquement stables assemblées à partir de nanoparticules de magnétite revêtues d'acide oléique (OA) en formulant le ferrofluide comme milieu d'évaporation qui participe au processus de piégeage cinétique. Nous examinons l'impact du champ magnétique inhomogène, la concentration de nanoparticules, le taux d'évaporation, le type de solvant et le substrat. Nous montrons que l'excès de ligand OA, de concert avec une réponse ferrohydrodynamique complexe, dirige les changements dans les modèles macroscopiques de l'ordre au désordre, et les transitions des modèles hexagonaux aux modèles labyrinthiques. Un polymère réticulant est introduit comme

système de réaction-diffusion où l'échange de matière en présence du champ appliqué induit un nouveau type de morphogenèse. Nous observons des hiérarchies d'ordre non signalées jusque-là allant du nanomètre au millimètre dans ces structures. Enfin, nous sondons les propriétés magnétiques des structures piégées par résonance ferromagnétique et magnétométrie. Dans le régime dilué, les nanoparticules magnétiques sphériques, cubiques et polydisperses sans interaction présentent des propriétés différentes de leurs homologues en interaction dans le système concentré de structures auto-organisées.

En conclusion, cette thèse fait progresser le paradigme de la formation de motifs, représentée par la réponse au champ magnétique des ferrofluides, dans de nouveaux aspects de la formation de motifs rendus possibles par la méthode de piégeage des nanoparticules de magnétite autoorganisées pour créer des structures hiérarchiques. La technique a une large portée en termes de modifications chimiques et physiques pour enquêter sur les principes fondamentaux de l'autoorganisation et peut-être pour créer des applications en aval des structures auto-organisées qui pourraient montrer des propriétés émergentes.

### Preface

It has long been reasonably conjectured that the striking macroscopic patterns exhibited by ferrofluids in a sustained magnetic field arise from the collective ordering of magnetic nanoparticles (MNPs) through the ferrohydrodynamic response of the medium. In conventional ferrofluids, these patterns disappear when the field is removed. In this thesis, we show that the MNPs are not just building blocks that sustain macroscopic patterns, but that astonishing hierarchies of order over many length scales can be "trapped" under reaction-diffusion conditions as permanent recordings that show surprising morphological complexity. Such complexity has eluded observation until now. Indeed, features of the patterns we observe find correspondence in biological and geological systems that evolve through the spatiotemporal coordination of building block elements like cells to make tissues, and hydrodynamically locked morphogenesis in karst and ice flutings. Moreover, we show that the encoded hierarchies of order from MNPs in our trapped features lead to new compositions and morphologies via solid-state thermal transformations. Our reaction-diffusion paradigms are based on irreversible MNP-ligand interlocking in evaporating alkanes and irreversible crosslinking of fluid polymer media that avoids parasitic MNP precipitation. Both systems lead to unusual but different types of morphology.

The main contributions of this thesis are the following:

 unveiling hierarchies of order evolving from nanoscale matter that have not been seen before;
 demonstration of how hierarchies of order can be used to prefigure new ordered structures with anisotropic properties with potential for advanced materials;

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3) simplicity and versatility of our methods to trap patterns from otherwise dynamic structures;

4) broader and more detailed justification of ferrofluids as models for self-organizing systems in general;

5) broadening of the discourse on field-directed self-organization from nanoparticles.

This thesis is based on research manuscripts that have been either published, submitted or are in preparation. The contributions of coauthors to each chapter are summarized below.

#### Chapter 2

Tianyu Zhong designed the experiments, carried out the nanoparticle synthesis and characterization, performed the patterning, wrote the script for image processing, analysis and manuscript writing. Jialin Meng assisted in patterning, project design, data analysis. Professor Mark Andrews contributed to data interpretation and manuscript preparation.

#### Chapter 3

Tianyu Zhong designed the experiments, carried out the nanoparticle synthesis and characterization, performed the patterning, analysis and manuscript writing. Matthew Burigana contributed to the synthesis of magnetite nanocubes, performed the patterning of the cube series and contributed to data interpretation. Jialin Meng helped with the sample characterization, data analysis and manuscript editing. Professor Mark Andrews contributed to data interpretation and manuscript preparation.

#### Chapter 4

This Chapter is adapted from "Zhong, T.; Fournier, P.; Dion, M.; Andrews, M. Permanent Encoding of Nano- to Macro-scale Hierarchies of Order from Evaporative Magnetic Fluids. *Nano Select.* 2021; 2: 591–599. https://doi.org/10.1002/nano.202000149"

Tianyu Zhong designed the experiments, carried out the nanoparticle synthesis and characterization, constructed the experimental setup and performed the patterning, analysis and manuscript writing. Professor Patrick Fournier contributed to data analysis and manuscript editing. Maxime Dion performed the magnetization measurements. Professor Mark Andrews contributed to project design, data interpretation and manuscript preparation.

#### Chapter 5

Tianyu Zhong designed the project, performed the FMR measurements, data processing, and manuscript writing. Professor Mark Andrews contributed to project design, data interpretation and manuscript preparation.

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# **List of Abbreviations**

2D	two dimensions
3D	three dimensions
AC	alternating current
BF	breath figure
BZ	Belousov–Zhabotinsky
DC	direct current
DPPH	2,2-diphenyl-1-picrylhydrazyl
EMR	electron magnetic resonance
EPR	electron paramagnetic resonance
ESR	electron spin resonance
FC	field cooled
FMR	ferromagnetic resonance
FT-IR	Fourier transform infrared spectroscopy
MNP	magnetic nanoparticle
MRI	magnetic resonance imaging
OA	oleic acid
RD	reaction-diffusion
RTV	room temperature vulcanized
SEM	scanning electron microscopy
SFM	superferromagnetic or superferromagnetism
SQUID	superconducting quantum interference device

SSG	superspin glass
TEM	transmission electron microscopy
VSM	vibrating sample magnetometer
ZFC	zero-field cooled

# List of symbols

Mc	critical magnetization
$M_{ m s}$	saturation magnetization
$\mu_0$	permeability of vacuum
μ	permeability of ferrofluid
ρ	density
g	gravitational constant
γ	interfacial tension
$\lambda_{c}$	characteristic wavelength
M	magnetization
$\Delta E$	free energy difference
$k_{ m B}$	Boltzmann constant
Т	temperature
$\mu_{\scriptscriptstyle  m B}$	Bohr magneton
e	elemental charge
ħ	reduced Plank constant
me	rest mass of electron
J	exchange constant
S	total spins
$V_{ m h}$	hydrodynamic volume
$\eta_0$	viscosity of fluid
$ au_{ m B}$	Brownian relaxation time

τn	Néel relaxation time
$ au_0$	time constant for Néel relaxation
Κ	anisotropy constant
V	volume of nanoparticle
Tb	blocking temperature
$ au_{m}$	measurement time
m	magnetic dipole moment
r	distance vector
$\lambda_{dd}$	dipolar coupling constant
d	sphere diameter
В	magnetic flux density
Н	magnetic field strength
H <sub>d</sub>	demagnetization field
${\mathcal N}$	demagnetization factor
χ	magnetic susceptibility
$K_1$	first order anisotropy constant
Hex	external magnetic field
Ea	anisotropy energy
Keff	effective magnetic anisotropy constant
Kv	volume anisotropy constant
S	surface of particle
g	g-value, or g factor
Ν	number of spikes
d	diameter of spikes
--------------------	--
h	height of spikes
λ	pattern wavelength
$\sigma$	standard deviation of wavelength
Svor	Voronoi entropy
Es	Surface energy
R	intensity ratio of the asymmetric and symmetric CH <sub>2</sub> stretching modes
Ias	intensity of the asymmetric stretching modes
Is	intensity of the symmetric stretching modes
Vas	frequency of the asymmetric stretching modes
Vs	frequency of the symmetric stretching modes
h	Planck's constant
ν	microwave frequency
С	concentration
$\Delta H_{ m pp}$	peak-to-peak linewidth
Hres	resonance field
Ha	anisotropy field
$K_{ m dd}$	dipolar interaction anisotropy
$\lambda_{\rm s}$	saturation magnetostriction coefficient
3	strain

# **Chapter 1 Introduction**

# 1.1 Morphogenesis in ferrofluids

Ferrofluids are colloidal suspensions of ~10 nm magnetic nanoparticles (MNPs) in a host liquid. Since their invention by Papell in the 1960s,<sup>1</sup> ferrofluids have attracted wide scientific interest because they exhibit peculiar fluid dynamics, rapid magnetic response and magnetically tunable optical and thermal properties. Applications of ferrofluids take advantage of their responses to magnetic fields. For one, ferrofluids can be used as tunable soft templates, since they can form a variety of patterns when exposed to magnetic fields. The patterns can be transferred to an immiscible prepolymer which can be solidified on the ferrofluid pattern, allowing an inverse pattern to be acquired. Polymer replicas obtained this way can be used to direct water flow.<sup>2</sup> Ferrofluids can also be used to guide self-assembly of nonmagnetic particles. Yellen et al. demonstrated a range of unique structures such as 'Saturn rings', 'flowers', 'poles', and 'two tone', which were assembled from simple nonmagnetic beads assisted by ferrofluids.<sup>3</sup> Later, Yin et al. applied this methodology to assemble polystyrene particles and silica particles to make photonic crystals.<sup>4, 5</sup> Ferrofluids of iron oxide nanoparticles have been used in biomedical applications for magnetic resonance imaging (MRI),<sup>6</sup> targeted hyperthermia,<sup>7</sup> and drug delivery.<sup>8</sup> Ease of separation with a magnetic field makes ferrofluids candidates for recyclable catalyst platforms and wastewater treatment agents.<sup>9, 10</sup> A comprehensive review of the applications of ferrofluids can be found in reference (11).

Note that dilute suspensions of MNPs (< 0.1 vol%) are generally not regarded as ferrofluids because the magnetization is weak at a low MNP concentration. Typically, MNPs are concentrated to be > 2 vol% in a ferrofluid to provide strong ferrohydrodynamic coupling between the MNP magnetization and the fluid dynamics.<sup>12</sup> In the presence of magnetic fields, a ferrofluid exhibits a range of steady-state morphologies at different length scales. Morphogenesis in ferrofluids results from self-organization of MNPs that involves interactions between MNPs and the fluid host. Morphogenesis, literally "the generation of form", is also referred to as pattern formation, appearance of order from a disordered system. Ferrofluid morphologies in principle span nano- to meso- to macro-scales. In the following sections, we explore the morphogenesis of ferrofluids at the macroscale in the presence of magnetic fields.



Figure 1.1 Rosensweig spike pattern in ferrofluids induced by a permanent magnet.

## 1.1.1 Rosensweig pattern

Shortly after Papell's invention in 1967, Rosensweig and Cowley discovered and studied pattern formation of ferrofluids.<sup>13</sup> Figure 1.1 shows the striking pattern formed in ferrofluids. In the

presence of a strong enough vertical *homogeneous* magnetic field, the ferrofluid surface can deform into peaks and valleys to yield a patterned lattice. The peak structures are generally referred to as *spikes*. Rosensweig developed a theory of ferrohydrodynamics to describe pattern formation in the frame of fluid mechanics.<sup>14</sup> The spike pattern is also known as the Rosensweig instability, or normal field instability because the field is applied normally.

The formation of the spike pattern is the result of competition between surface tension, gravity, and magnetic force. **Figure 1.2** depicts how the instability arises: the ferrofluid surface is under magnetic induction but stabilized by gravity and surface tension. When the applied field is strong enough, any fluctuation, which is always present, at the fluid surface will be captured instantaneously by the field flux lines. The surface deforms as it alters the magnetic flux lines around it. Each spike creates its own local magnetic field that repels other spikes. The balance of dipole-dipole attraction within spikes and repulsion between spikes leads to a steady-state pattern at the macroscale. The onset of the Rosensweig pattern at the critical magnetization  $M_e$  usually gives rise to a hexagonal array of peaks. When the applied magnetic field increases to a second threshold, the hexagonal pattern can transition to a square array.<sup>15-17</sup> The transition between hexagonal and square pattern may give rise to hepta-penta defects in the pattern. This kind of defect is observed in our system in Chapter 3.



**Figure 1.2** Schematic of magnetic field lines compressed and uncompressed by the peak and the valley of a ferrofluid surface. Adapted from reference (*18*), copyright (2009) Springer.

A prototypical ferrofluid consists of ~10 nm magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles suspended in a nonvolatile hydrocarbon like kerosene. Patterning occurs when a critical magnetic field is reached. This critical field depends on the composition of the ferrofluid. According to Rosensweig's linear analysis,<sup>14</sup> the critical magnetization  $M_c$  is given by

$$M_c^2 = \frac{2}{\mu_0} \left( 1 + \frac{\mu_0}{\mu} \right) \sqrt{\rho g \gamma}$$
(1.1)

Here  $\mu_0$  is permeability of vacuum,  $\mu$  is the permeability of the ferrofluid,  $\rho$  is the density, g is the gravitational constant and  $\gamma$  is the interfacial tension. The macroscopic pattern can be characterized by its wavelength, which is the peak to peak distance among the spikes. The characteristic wavelength is given by:

$$\lambda_c = 2\pi \sqrt{\frac{\gamma}{\rho g}} \tag{1.2}$$

Interestingly, the wavelength depends only on the material properties of the ferrofluid, i.e. the magnetic field strength cannot change the wavelength of the pattern. Later in Chapter 2, we will

show how the wavelength is actually tunable in different *inhomogeneous* magnetic fields. When the applied magnetic field is inhomogeneous, field gradients impose magnetic forces that are in the same direction as gravity. The magnetic force due to a non-uniform magnetic field acting on a sample is given by:

$$F_m = \nabla(\mu_0 \boldsymbol{H} \cdot \boldsymbol{M}) \tag{1.3}$$

where *H* is the applied magnetic field. This magnetic force can be much larger than gravity. Recently, Timonen et al. used a permanent magnet to perturb ferrofluid droplets on a superhydrophobic surface (**Figure 1.3A**).<sup>19</sup> In their system, Rosensweig instability manifests as a mother droplet splitting into a patterned array of daughter droplets (**Figure 1.3C**). The splitting criterion is given by a characteristic wavelength  $\lambda_c$ 

$$\lambda_{\rm c} = 2\pi \sqrt{\frac{\gamma}{d(\mu_0 MH)/dz}} \tag{1.4}$$

where  $\gamma$  is surface tension, *M* is magnetization and *H* is the applied magnetic field. A ferrofluid droplet will split when its diameter is larger than the characteristic wavelength  $\lambda_c$  (Figure 1.3B). Equation 1.4 implies that the wavelength depends on the magnetic field gradient. In fact, Equation 1.4 is not just a criterion for spike fission. In Chapter 2, we will show that this wavelength also applies to determining the pattern wavelength.



**Figure 1.3** (A) Schematic of ferrofluid droplet shape under influence of a cylindrical permanent magnet. (B) Droplets split when the diameter *d* is larger than  $\lambda_c$ , where  $\lambda_c$  is field dependent given by Equation 1.4. (C) Examples of ferrofluid droplet splitting from one mother droplet to seven daughter droplets. Reprinted with permission from reference (*19*), copyright (2013) American Association for the Advancement of Science.

### 1.1.2 Labyrinthine pattern

The labyrinth is another kind of pattern that a ferrofluid can form, though it is not exclusive to ferrofluids. When a ferrofluid mixed with an immiscible nonmagnetic fluid is placed between two closely spaced glass plates (Hele-Shaw cell configuration), a labyrinthine pattern forms in a vertically applied magnetic field. Labyrinth formation is governed by dipolar interactions and interfacial tensions and can also be found in its dielectric counterparts (see **Figure 1.4A**). In 1983, Rosensweig et al. used an energy minimization analysis to predict the labyrinth spacing and concluded that labyrinthine patterns are *at equilibrium*.<sup>20</sup> In actuality, the labyrinthine structure is the outcome of a response at a steady state. Ten years later, Goldstein et al. revisited the topic in

the framework of a "dynamic theory".<sup>21</sup> They showed that an identical starting configuration of ferrofluids can yield different final states under the same magnetic field (**Figure 1.4B**). These equivalent states are non-equilibrium steady states in a global energy landscape. Moreover, the pathways—pattern formation processes—are sensitive to fluctuations. This is precisely a property manifested by non-equilibrium structures. Their work reflects the non-equilibrium nature of the labyrinthine structures. In Chapter 3, we present another way to create labyrinthine patterns, which may in turn indicate the dynamic nature of ferrofluid systems. Ferrofluid morphologies can be understood in the frame of non-equilibrium structures.



**Figure 1.4** (A) Labyrinthine patterns in magnetic and dielectric fluids enclosed in Hele-Shaw cells. The applied field intensity and the gap spacing are indicated. Reprint with permission from reference (*20*), copyright (1983) Elsevier. (B) Shape evolution of three ferrofluid circles in a Hele-Shaw cell in the presence of a magnetic field and their energy relaxation over time. Three nearly identical initial conditions a, b and c generate three different outcomes. Reprinted with permission from reference (*21*), copyright (1993) American Association for the Advancement of Science.

### 1.1.3 Non-equilibrium systems and dissipative structures

Physical systems that operate under non-equilibrium conditions have attracted attention in recent years. To some degree research in this area has been stimulated by interest in *emergent* properties of such systems. By "emergent", we mean new properties that their constituting parts do not possess. Emergence can be seen as the result of self-organization under non-equilibrium conditions and constant exchange of energy and matter to sustain the organization. When the exchange stops, the steady states relax back to equilibrium and the emergent properties perish. It was Prigogine first who put forward this notion framed in terms of what is called *dissipative structures*.<sup>22-27</sup> Dissipative structures exist in non-equilibrium steady states that are sustained when a constant flow of energy and matter is exchanged in a thermodynamic open system.

Dissipative (dynamic) structures can be identified in colloidal microparticle suspensions. Granick et al. presented a general strategy to reconfigure metal-dielectric Janus particles by a changing electric field to yield various ordered or dynamic structures including swarms, chains, clusters, waves and vortices.<sup>28</sup> Snezhko et al. showed that ferromagnetic particles self-assemble into localized clusters in an alternating magnetic field. These dynamic structures can capture, transport, and position nonmagnetic particles by applying an additional small magnetic field.<sup>29, 30</sup> Note that the alternating electric and magnetic fields in these examples are the driving forces for the formation of dissipative structures.

Spatial patterns can arise in dissipative structures. The Rayleigh–Bénard instability yields dissipative patterns when a confined thin layer of fluid heated from below. The heat, or the resulting temperature gradient, drives the fluid to a convective state, forming hexagonal or striped

patterns (**Figure 1.5A**). Another example is the Belousov–Zhabotinsky (BZ) reaction. It represents a class of oscillating chemical reactions involving a number of intermediates that couple with diffusion in the medium. The coupled events produce complex wave and spiral patterns (**Figure 1.5B**). The BZ reaction has become a symbol for non-equilibrium chemical systems and several studies have been carried out to investigate its relationship to Turing patterns under nonequilibrium conditions.<sup>31-33</sup>



Figure 1.5 (A) Examples of roll and hexagonal patterns in a Rayleigh–Bénard system. Reprinted with permission from reference (*34, 35*), copyright (1991) and (1993) American Physical Society.
(B) Dynamic evolution of the BZ pattern. Reprinted with permission from reference (*36*), copyright (1984) Nature Publishing Group.

How does one determine non-equilibrium states? As adapted from Hermans et al.,<sup>37</sup> **Figure 1.6A** identifies different states of assemblies in a free energy landscape. The thermodynamic equilibrium state **#1** resides in the global minimum. Ferrofluids in the absence of an applied magnetic field are at thermodynamic equilibrium. A dissipative state requires an exchange of energy or matter with the environment to maintain it. This corresponds to **#4** in **Figure 1.6B**. This non-equilibrium state

might represent how a particular ferrofluid pattern requires an applied magnetic field to sustain it. Interestingly, one may reach a non-dissipative non-equilibrium state from a dissipative state or by other pathways. This non-equilibrium state does not require an exchange of energy/mass to sustain because it is metastable #3 ( $\Delta E \approx k_B T$ ) or kinetically trapped #2 ( $\Delta E \gg k_B T$ ). But its formation depends on preparation sequence and conditions. This is precisely the pathway we take in this thesis to study our ferrofluid patterns from fugitive solvent media. This thesis explores what can be learned by trapping ferrofluid patterns as permanent replicas of how the MNP building blocks couple with the applied magnetic field. In Chapter 2, we trap the classic spike pattern and show that the trapping result depends sensitively on the conditions of experiment.



**Figure 1.6** Identification of different thermodynamic states of assemblies. (A) Different thermodynamic states in a Gibbs free energy landscape. (B) Questions posed to identify the unknown states. Reproduced from reference (*37*), copyright (2017) Royal Society of Chemistry.

### 1.1.4 Self-organization and self-assembly

While concepts of "self-organization" and "nanoparticle" were undeveloped when Rosensweig and coworkers discovered ferrofluid patterns, we now understand that pattern formation in ferrofluids is related to self-organization of MNPs in an applied magnetic field. In this section, we distinguish self-organization from self-assembly. We make a distinction because the literature is often unclear about the definitions, and the terms are sometimes wrongly used interchangeably. By custom, self-assembly is frequently used in the field of chemistry, whereas self-organization is often encountered in biology. "Self-organization" is similar to the term "dynamic self-assembly" described by Whitesides and Grzybowski,<sup>38</sup> and the term "non-equilibrium assembly" has been used in some recent publications.<sup>39-41</sup> A consistent definition of the two terms is needed for efficient communication across disciplines.

Both self-assembly and self-organization refer to processes in which order of structures (patterns, for example) can be traced to fundamental building blocks. Despite the building block origins, self-assembly and self-organization are fundamentally different: self-organization refers to order that arises under non-equilibrium conditions. Self-assembly is associated with systems approaching and/or residing at thermodynamic equilibrium.<sup>42</sup>

Self-assembly results in a final structure residing in free energy minimum. The self-assembled structure is prefigured by the intrinsic properties of the initial system, i.e. the size, shape and type of building blocks, and strength of interactions among building blocks. In nanoparticle systems, forces among particles have different magnitudes, with scalar relationships that depend on the interparticle distance *r*, proportional to 1/r,  $1/r^2$ ,  $1/r^3$  and  $1/r^6$  for electrostatic, hydrogen bonding,

dipole-dipole and van der Waals interactions, respectively.<sup>43</sup> The resulting structures may emerge as highly symmetric close-packed patterns of the building blocks, typically in hcp and bcc arrangement. Examples of self-assembly can be found in the rich set of nanoparticle systems, e.g. mesocrystals of self-assembled spherical and cubic magnetic nanoparticles,<sup>44</sup> and binary nanoparticle superlattices of MNPs of different sizes.<sup>45</sup>

In contrast, self-organization entails dissipative non-equilibrium steady states at macroscopic levels. The dissipative non-equilibrium steady states are characterized by self-organized structures that decay and disappear once energy and/or matter input has ceased. These states arise due to collective interactions among multiple building blocks.<sup>42</sup> The collective interaction of the building blocks is long-range in character. The response of building blocks to external forces is coupled with intrinsic forces in building blocks. It is the self-organization that gives rise to hierarchies of order at multiple length scales. Self-organizing systems are thermodynamically open—they exchange energy and matter with the environment. For example, ferrofluids form hexagonal patterns at the macroscale (**Figure 1.1**), resulting from the self-organizing magnetic nanoparticles directed by an external magnetic field. The pattern, or the self-organizing MNPs, collapses once the field is removed.

Arango-Restrepo and coworkers have offered a mapping that runs from self-assembly to selforganization through a "nonequilibrium self-assembly" term.<sup>46</sup> **Figure 1.7** illustrates some relations between self-organization and nonequilibrium self-assembly. Indeed, self-organization and self-assembly may coexist in ferrofluids. MNPs with strong dipolar interactions can selfassemble into chains in the absence of a magnetic field. This tendency will be discussed in Section 1.2.6 in details. When MNPs are subject to an external magnetic field, self-assembled chains may continue to organize into 2D and 3D structures. Nonetheless, self-organization may give rise to non-close-packed superstructures and complex patterns over many length scales.<sup>47, 48</sup> This is evident in the mapping in **Figure 1.7**. High structural complexity may originate in the spatial and temporal coupling of different interactions at the nanoscale. This characteristic of self-organization was first captured by Turing's reaction-diffusion (RD) model.<sup>49</sup> The revolutionary idea of the RD model is the inclusion of a "reaction" between the diffusing elements. Despite its simplicity, the RD model allows us to extract features of more complex systems.<sup>50</sup> In Chapter 4, we will employ the idea of reaction-diffusion in ferrofluids and explore how it leads to new kinds of patterning.



**Figure 1.7** Structure formation in self-organization and nonequilibrium self-assembly by dissipating energy or energy and matter. Examples are given in dashed squares. Reprint with permission from reference (*46*).

# 1.2 Magnetic nanoparticles

Now let us turn to the essential component of ferrofluids—magnetic nanoparticles. Magnetic nanoparticles are commonly made from Fe,<sup>51</sup> Co,<sup>52</sup> FePt,<sup>53</sup> iron oxides,<sup>54</sup> and ferrites,<sup>55</sup> among others. Iron oxide nanoparticles are the most widely explored MNPs to date. This is due to their low toxicity and good chemical stability, compared with formally zerovalent metallic nanoparticles (Fe, Co, Ni).

#### 1.2.1 Iron oxide nanoparticles

Iron oxide nanoparticles are typically represented by two predominant magnetic forms: magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). Magnetite nanoparticles are partially oxidized in air and therefore most magnetite nanoparticles contain surface maghemite. This oxidation can be visualized by the color change from black to brown. The magnetization of iron oxide nanoparticles is size-dependent: the larger the size, the larger the saturation magnetization. But the saturation magnetization of iron oxide nanoparticles is always smaller than its bulk phase magnetization ~92 emu/g.



**Figure 1.8** The crystal structure of inverse spinel magnetite (Fe<sub>3</sub>O<sub>4</sub>), adapted from reference (*56*), copyright (2007) IOP Publishing.

The crystal structure of magnetite (Fe<sub>3</sub>O<sub>4</sub>) belongs to the class of inverse spinel. Its formula can be written as  $[Fe^{3+}][Fe^{2+}Fe^{3+}]O_4$ , where the left bracket denotes tetrahedral sites that contain only trivalent iron and the right bracket denotes octahedral sites with mixed divalent and trivalent iron (**Figure 1.8**). Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) has a crystal structure similar to that of magnetite. The major difference is that most iron cations are trivalent, if not all. Cation vacancies present in the octahedral sites compensate for the missing divalent iron Fe<sup>2+</sup>. The missing Fe<sup>2+</sup> accounts for the fact that the saturation magnetization of maghemite is smaller than magnetite.

### 1.2.2 Why are iron oxides magnetic?

To understand why magnetite is magnetic, let us briefly return to some fundamentals of magnetism. The magnetic properties of materials originate mainly from the magnetic moment of electrons, as the nuclear magnetic moment is typically smaller than that of electrons by three orders of magnitude. The magnitude of the magnetic moment of an electron is given in terms of the Bohr magneton  $\mu_{\rm B}$ :

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} A \, m^2 \tag{1.5}$$

where *e* is the elemental charge,  $\hbar$  is the reduced Plank constant and  $m_e$  is the electron rest mass. The direction of the magnetic moment is determined by the spin. The spin of an electron can only be one of two states,  $\pm 1/2$  or  $\pm 1/2$ , sometimes "up" or "down". Depending on the arrangement of spins, the magnetism of materials can be classified into two categories: paramagnetism or diamagnetism. Paramagnetic materials are attracted to magnetic fields, whereas diamagnetic materials are repelled by magnetic fields. Paramagnetism can be further divided into ferromagnetism, ferrimagnetism and antiferromagnetism based on the arrangement of spins within the crystal structures of the materials. **Figure 1.9** illustrates the different kinds of magnetism that are commonly encountered.



**Figure 1.9** Different kinds of magnetism and their spin arrangements. Ferromagnetism arises when all spins are parallelly aligned. Ferrimagnetism occurs when the magnitude of parallel spins and antiparallel spins do not match, whereas antiferromagnetism refers to two spin states that cancel each other completely. In general terms, the spins in paramagnets are randomly oriented but will be aligned by an external magnetic field. Diamagnets have all electrons paired, therefore they repel the magnetic field.

When atoms are brought together to form matter, *exchange interactions* determine whether the electron spins are parallel or antiparallel. The exchange interaction is represented in quantum mechanical terms as occurring between two adjacent identical atoms, as can be formulated via the Heisenberg exchange Hamiltonian:<sup>57</sup>

$$\mathcal{H} = -2\mathcal{J}\mathbf{S}_i \cdot \mathbf{S}_i \tag{1.6}$$

Here  $\mathcal{J}$  is the exchange constant,  $S_i$  and  $S_j$  are total spins of the two atoms. When  $\mathcal{J}$  is positive, parallel spins are favored. This gives rise to ferromagnetism, where (unpaired) spins are all parallel (e.g. Fe, Co). When  $\mathcal{J}$  is negative, spins are antiparallel and antiferromagnetism arises.

Exchange interactions are short ranged for identical atoms. In a crystal lattice, *double exchange* and *superexchange* are indirect interactions that are mediated by intermediary atoms like oxygen.

Double exchange implies that an electron may be exchanged between cations in different oxidation states. In the case of mixed valence magnetite, an electron can be exchanged between  $Fe^{3+}-O-Fe^{2+}$  and  $Fe^{2+}-O-Fe^{3+}$  via a symmetry adapted p-orbital on oxygen. This is the origin of the so-called double exchange<sup>58</sup> The lowest energy of such systems corresponds to a parallel alignment of the spins in the two Fe ions, giving rise to ferromagnetism (**Figure 1.10A**). Superexchange refers to another electron exchange mechanism in two identical cations via an intermediary anion.<sup>59, 60</sup> For instance, the  $Fe^{3+}-O-Fe^{3+}$  180° configuration favors an antiferromagnetic interaction where the spins are antiparallel (**Figure 1.10B**). In other cases, ferromagnetic interaction may be favored when the cation-anion-cation geometry is configured at 90°.



**Figure 1.10** Long-range exchange mechanism. (A) Double exchange gives rise to ferromagnetism. (B) Super-exchange that accounts for antiferromagnetism. These two exchange interactions account for the magnetism in magnetite (Fe<sub>3</sub>O<sub>4</sub>).

### 1.2.3 Superparamagnetism

In ferrofluids, magnetic nanoparticles (MNPs) have typical dimensions below 20 nm. In this size range MNPs are single domain, meaning that all local atomic magnetic moments are parallel in a single nanoparticle. These single domain MNPs can be treated as "*macrospins*". In colloidal suspensions, the magnetization of MNPs will relax (re-orient) to a new direction when the external applied field changes. The relaxation occurs via two mechanisms. The first mechanism is due to Brownian relaxation: particles rotate physically. The characteristic Brownian relaxation time is given by:

$$\tau_{\rm B} = \frac{3V_{\rm h}\eta_0}{k_{\rm B}T} \tag{1.7}$$

where  $V_h$  is the hydrodynamic volume of the nanoparticle,  $\eta_0$  is the viscosity of the fluid medium. Increasing  $\eta_0$  raises  $\tau_B$ , so fixing MNPs in a solid host should suppress this pathway.

The second mechanism is the Néel relaxation: the magnetic spin flips between its two opposite directions along the easy axis of magnetization within the particle. This occurs when the thermal energy  $k_{\rm B}T$  is larger than the energy barrier *KV*, the magnetic anisotropy energy of MNPs. The characteristic Néel relaxation time is given by:

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \tag{1.8}$$

Where  $\tau_0$  is a time constant typically in the order of  $10^{-9}$  s, *K* is the anisotropy constant of the material, *V* is the volume of the nanoparticle. When the size of an MNP decreases sufficiently, its anisotropy energy *KV* may be smaller than the thermal energy  $k_BT$ . The magnetization of nanoparticles fluctuates according to the mean thermal energy. In this case, and in the absence of an applied magnetic field, the overall magnetization of the collection of MNPs is zero. MNPs in

this regime are *superparamagnetic*. The superparamagnetic size limit for magnetite nanoparticles is typically associated with diameters under 17 nm.<sup>61, 62</sup> Ferrofluids of superparamagnetic MNPs therefore show no magnetization at zero fields, when MNPs are randomly distributed in a fluid host. This is the thermodynamic equilibrium state for ferrofluids.

Now, lowering the temperature T may bring  $k_BT$  below KV. The MNPs are then said to be "blocked". At the blocking temperature  $T_b$ , the magnetic moments of MNPs may appear to be static on the time scale of measurement. Rearranging Equation 1.8 one may estimate the blocking temperature:

$$T_b = KV/k_B \ln(\tau_m/\tau_0) \tag{1.9}$$

where  $\tau_m$  is the measurement time depending on the experimental technique. Typically,  $\tau_m$  ranges from 10–10<sup>2</sup> s for magnetization measurements. We estimate *K* of MNPs with this equation in Chapter 5.

### 1.2.4 Synthesis of iron oxide nanoparticles

Synthesis of monodisperse iron oxide nanoparticles has advanced since the early 2000s as understanding and techniques of separating nucleation and growth processes matured and was applied to different preparation methods.<sup>63</sup> The methods selected to make iron oxide nanoparticles can greatly affect size distribution, shape, crystallinity, surface chemistry and magnetic properties. The predominant synthetic approaches are those that use coprecipitation, microemulsions, thermal decomposition or hydrothermal synthesis. **Table 1.1** summarizes the main differences among them. In this thesis, we use coprecipitation and thermal decomposition. The procedures are briefly outlined next.

Method	Reaction	Reaction	Reaction	Size	Shape	Yield
	condition	temperature	time	distribution	control	
Coprecipitation	inert or air	20–90 °C	minutes	medium	poor	High/scalable
Microemulsion	Inert or air	20–80 °C	hours	narrow	good	low
Thermal decomposition	inert	200–350 °C	hours	narrow	excellent	High/scalable
Hydrothermal synthesis	high pressure	150–220 °C	hours- days	narrow	good	High/scalable

Table 1.1 Comparison among synthetic methods of iron oxide nanoparticles.<sup>63</sup>

### Coprecipitation

Pioneered by Massart in 1981,<sup>64</sup> coprecipitation has been widely studied and is now commonly used. Coprecipitation requires an aqueous base to precipitate magnetite from a solution of ferric and ferrous ions. The overall reaction is:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O_4$$

Many reaction parameters can be adjusted to control the size distribution and crystallinity of the nanoparticles. These parameters have been well studied, including the ratio of Fe<sup>3+</sup>/Fe<sup>2+</sup>, choice of anion, choice of base, precipitation temperature, aging temperature, atmospheric conditions, stirring mechanics and ionic strength.<sup>63</sup> The synthesis may be adapted to include post-treatment options to improve colloidal stability. For instance, oleic acid (OA) added to the reaction mixture after the addition of base yields hydrophobic nanoparticles that can be dispersed in nonpolar solvents. Post-treatment with citric acid yields nanoparticles that are hydrophilic and therefore water dispersible. By coprecipitation, one can make grams of magnetite nanoparticles within hours.

The resulting nanoparticles offer high saturation magnetization and are stable under ambient conditions. The main drawback of coprecipitation is lack of nanoparticle size and shape control.

#### Thermal decomposition

Thermal decomposition can overcome the problem of size and shape control. This method involves the decomposition of precursor organometallic compounds in high-boiling point solvents at high temperatures. The organometallic precursors can be iron pentacarbonyl, iron acetylacetonate (iron(3+);(Z)-4-oxopent-2-en-2-olate), iron oleate (iron(3+);(Z)-octadec-9-enoic acid), among others.<sup>65</sup> Oleic acid, oleylamine and other fatty acids are often used as stabilizing ligands in the synthesis. In fact, a study shows that the iron-oleate is a crucial intermediate in the synthesis of highly monodisperse iron oxide nanoparticles.<sup>66</sup> Synthesis of monodisperse nominally magnetite nanoparticles was described by Park et al. in 2005.<sup>67</sup> They reported that grams of magnetite nanoparticles can be prepared by thermal decomposition of iron oleate in octadecene with oleic acid as a stabilizing ligand at 320 °C. The reaction is represented by:

$$\operatorname{FeCl}_3 + \operatorname{Na}(\operatorname{C}_{17}\operatorname{H}_{33}\operatorname{COO}) \to \operatorname{Fe}(\operatorname{C}_{17}\operatorname{H}_{33}\operatorname{COO})_3 \xrightarrow{\Delta} \operatorname{Fe}_3\operatorname{O}_4\operatorname{NPs}$$

The Park method fell short of experimental details, making it difficult to reproduce the findings. A later study showed that nanoparticles obtained by the Park method are actually mixed with nonmagnetic phase wüstite (FeO). The presence of FeO decreases the saturation magnetization of the nanoparticle samples produced this way. Recently, Kemp et al. showed that exposure of the reaction to 1% oxygen in argon oxidizes the nanoparticles to pure magnetite (Fe<sub>3</sub>O<sub>4</sub>) directly in the reaction mixture, improving their saturation magnetization.<sup>68</sup> In Chapter 3, we describe a simple trick to transform the wüstite phase into magnetite.

In summary, when polydispersity of MNPs is not a major concern, coprecipitation can provide a simple pathway to obtain large quantities of MNPs. On the other hand, monodisperse MNPs are essential when studying their fundamental properties, where the effects of their size and shape can be directly related to observed properties.

### 1.2.5 Surface ligands on iron oxide nanoparticles

The surface energy of iron oxide nanoparticles is very high. Strong attractions among MNPs may lead to uncontrolled aggregation and precipitation. Iron oxide nanoparticles are therefore often surface modified to add repulsive forces to balance the attractive forces. Nanoparticles may be stabilized by ligating long-chain molecules to their surfaces to create repulsive steric forces. Ligands can be introduced during the synthesis of nanoparticles or added after synthesis via surface modification (ligand exchange). Suitable ligands contain one or more head groups that have a high affinity for iron oxide surfaces, e.g., carboxyl (–COOH), hydroxyl (–OH), phosphonyl (–PO(OH)2), and amine (–NH2) groups.<sup>69, 70</sup>

A common ligand is oleic acid (OA,  $C_{18}H_{34}O_2$ ), and its anion form oleate (OA<sup>-</sup>). The carboxylate head group binds to the iron atoms of the nanoparticles through bidentate chelate, bidentate bridging and monodentate coordination (**Figure 1.11**).<sup>71</sup> The double bond "kink" in OA weakens the close packing between the OA long chains and therefore favors their solvation in nonpolar solvents. This is confirmed by the fact that stearic acid, a saturated acid ( $C_{18}H_{36}O_2$ ) with the same chain length is a poor stabilizer for iron oxide nanoparticles.<sup>72</sup> Formation of stable superstructures of colloidal particles has been linked to ligand-ligand interactions. It was proposed that ligands on nanoparticle surface are "soft", meaning that the ligand corona can deform when nanoparticles are in contact during the assembly process. As a result, the gap between two nanoparticles in the superstructure is close to the length of the ligand.<sup>73</sup> For oleic acid capped iron oxide nanoparticles, the interparticle distance between two MNPs is  $\sim$ 2 nm. In this case, the superstructure of nanoparticles is stabilized by ligand interdigitation. In Chapter 3, we shall take a closer look at the binding of OA in the superstructure and also show that OA can do more than just stabilize nanoparticles.



**Figure 1.11** Possible binding modes of oleate to the surface of magnetite nanoparticles. Upper is bidentate chelate, center is bidentate bridging and lower is monodentate coordination.

## 1.2.6 Magnetic dipole-dipole interaction

Interparticle interactions between MNPs include through-space exchange interaction and dipolar interactions. The exchange interaction is usually negligible since most MNPs are coated with stabilizing ligands. Therefore, only the dipolar interaction is operative in a self-organizing MNP

system. The magnetic dipole-dipole energy of interaction between two spherical magnetic nanoparticles is given by:

$$E_{dd} = \frac{1}{4\pi\mu_0} \left[ \frac{\boldsymbol{m_1} \cdot \boldsymbol{m_2}}{r^3} - \frac{3(\boldsymbol{m_1} \cdot \boldsymbol{r})(\boldsymbol{m_2} \cdot \boldsymbol{r})}{r^5} \right]$$
(1.10)

Here  $\mu_0$  is vacuum permeability,  $m_1$  and  $m_2$  are the magnetic dipole moments of the two nanoparticles, r is the distance vector from  $m_1$  to  $m_2$ , and r its magnitude. The dipole-dipole interaction can be attractive or repulsive, depending on the relative directions between the dipoles. The right panel of **Figure 1.12** illustrates how magnetic dipoles attract or repel each other in an applied magnetic field.



**Figure 1.12** Schematic illustration of dipolar interactions between magnetic nanoparticles. In the absence of an applied field H = 0, MNPs are randomly oriented. But the dipoles may interact with one another if dipolar coupling constant  $\lambda_{dd} > 2$ . An applied field H directs assembly of MNPs into chains. The dipolar interaction between MNPs can be attractive or repulsive, depending on the relative positions of MNPs. The blue regions denote attraction and the red regions repulsion. Adapted with permission from reference (74), copyright (2009) Wiley.

The dipolar coupling constant  $\lambda_{dd}$  can be used to predict the self-assembly behavior of MNPs. It is given by the ratio of dipolar interaction energy to thermal energy:

$$\lambda_{dd} = \frac{m^2}{d^3 k_B T} \tag{1.11}$$

where *m* is the magnetic moment of MNPs, *d* is the hard sphere diameter of the MNPs,  $k_B$  is the Boltzmann's constant and *T* is the temperature. One can observe spontaneous dipolar interaction when the dipolar potential exceeds thermal fluctuations. For a dipolar coupling constant  $\lambda_{dd} < 2$ , MNPs self-assemble into isotropic "islands" in zero field (most likely due to van der Waals attractions). For  $\lambda_{dd} > 2$ , MNPs can self-assemble into flux-closure rings,<sup>75</sup> chains and in the absence of a magnetic field.<sup>76, 77</sup> Self-assembly of MNPs into chains is confirmed by experiments and simulations.<sup>78-82</sup>

When a magnetic field is applied, MNPs can organize into chains, sheets and mesocrystals with a long-range order (left panel in **Figure 1.12**). The orientation of the self-organized structures is governed by the direction of the applied magnetic field.<sup>83</sup> The internal magnetic field of the self-organized structures can be extended with dipolar interactions among the MNPs, giving rise to ferromagnetic or antiferromagnetic behavior.<sup>84</sup> This is in contrast to the superparamagnetic nature of the individual MNPs, where the net magnetization is zero. The collective magnetic properties of self-organized superstructures of MNPs will be investigated in Chapter 5.

# 1.3 Common assembly strategies

A stable colloidal suspension of nanoparticles is a common starting point for assembly. The experimental techniques for assembly fall into two major categories: evaporation and destabilization of the nanoparticle colloidal suspension.

### 1.3.1 Solvent evaporation

Solvent evaporation plays an important role in pattern formation in this thesis. It is widely used to prepare nanoparticle superlattices. The term *evaporation induced self-assembly* is commonly used in the literature to describe this mode of assembly.<sup>85</sup> With evaporation driven assembly, a colloidal suspension of nanoparticles deposits onto a solid substrate, or a non-miscible liquid underlayer. The evaporation rate can be controlled by covering the nanoparticle suspension partially, or tilting the solid support, or regulating the solvent content of the atmosphere. Ordered superlattices may be obtained by controlling the solvent type, addition of excess ligands or slowing the evaporation rate. It should be noted that evaporation is strictly a non-equilibrium irreversible process.<sup>70</sup> The resulting structures are frequently kinetically trapped. Dynamics and fluctuations associated with evaporation can influence assembly at the nanoscale.<sup>86</sup> The most well-known evaporation induced flows are capillary flows and Marangoni flows,<sup>87-89</sup> both of which will affect the assembled structures at the macroscale after evaporation. In Chapter 2, we will examine the effects of evaporation on ferrofluid pattern formation.

### 1.3.2 Destabilization

Destabilization-mediated assembly occurs in suspensions when attractive interactions between nanoparticles exceed the repulsion forces provided by the interaction between the capping ligand and solvent. This can be achieved by adding a "poor" solvent to a stable nanoparticle solution in a "good" solvent in order to induce flocculation. In practice, the poor solvent needs to be delivered slowly to avoid rapid flocculation that otherwise would suppress ordering. Bergström et al. demonstrated that self-assembly of iron oxide nanocubes into mesocrystals with long-range order is induced by poor solvent enrichment.<sup>44</sup> Adding miscible additives to the solution to induce *depletion attraction* is an alternative approach. Manna et al. showed that CdSe/CdS nanorods assemble into 2D sheets from suspension due to depletion attraction by adding excess ligands.<sup>90</sup> In Chapter 3, we suggest how depletion attraction induced by excess OA may impact self-organization of MNPs.

### 1.3.3 Magnetic field directed assembly

External fields may be applied to regulate nanoparticle ordering. Assembly is directed by forces associated with external fields like electric, magnetic, light, flow fields and by interactions with surfaces like confining geometries and prepatterned interfaces.<sup>48</sup> Application of an external field is a convenient way to impose non-equilibrium conditions to direct nanoparticle assembly. This is because fields can be manipulated dynamically and switched on and off. Velev and coworkers fabricated microwires by electric field-directed assembly of 15–30 nm gold nanoparticles.<sup>91</sup> Prasad et al. studied chains of oriented magnetic nanoparticles assembled in the presence of a magnetic field.<sup>92</sup> Grzybowski et al. demonstrated that self-assembly of gold nanoparticles can be controlled by light through the photo-induced isomerization of azobenzene moieties in the nanoparticle surface ligands.<sup>93, 94</sup>

Among commonly used field-directed methods, magnetic intervention stands out for the following reasons. First, because free magnetic monopoles do not exist, magnetic interactions can be highly cooperative over a long range. This is in contrast to electric charge interactions that fall off at long distance due to the screening effect.<sup>95</sup> Second, a magnetic field has a higher energy density than its electric counterpart. An electric field of 40 kV cm<sup>-1</sup> can break down charges in particle suspension, while the energy-comparable magnetic field is 14 mT, which is quite small (A refrigerator magnet has a magnetic field of around 10 mT). Third, magnetic fields can be applied over a distance in the medium of air or liquids, whereas electric fields require conducting media. Light can be limited by scattering and absorption loss. In this thesis, we use evaporation combined magnetic fields to organize MNPs into superstructures.

# 1.4 Magnetic properties characterization

Properties of magnetic materials typically involve measurements of magnetic moments and magnetic anisotropy. These can be determined through magnetometry and ferromagnetic resonance (FMR). This section introduces concepts relevant to Chapter 5. Let us first get acquainted with some basic terminology used in magnetic characterizations.

### 1.4.1 Magnetic fields

The magnetic field is often encountered in two forms, B and H. The first definition of the magnetic field is associated with electromagnetic induction. The B field is equally referred to as the magnetic flux density. The sources of the B field are moving charges and flowing electric currents in conductors that create magnetic moments. The H field is known as the magnetic field strength. In a vacuum B and H are simply related by

$$\boldsymbol{B} = \boldsymbol{\mu}_0 \boldsymbol{H} \tag{1.12}$$

where the vacuum permeability  $\mu_0 = 4\pi \times 10^{-7}$  V s A<sup>-1</sup> m<sup>-1</sup>. The units of *B* are given in Tesla: T = V s m<sup>-2</sup>. In vacuum, B = 1 T, which corresponds to  $H = 10^4$  Oersted (Oe). The unit of *H* is given in Oe in the cgs system and in A m<sup>-1</sup> in the SI system. They are related by 1 Oe =  $(10^3/4\pi)$  A m<sup>-1</sup> = 79.59 A m<sup>-1</sup>. Both the *B* field and *H* field are commonly encountered in the literature. The *B* and *H* fields are related by the vacuum permeability  $\mu_0$  and the magnetization of the medium *M* 

$$\boldsymbol{B} = \mu_0 (\boldsymbol{H} + \boldsymbol{M}) \tag{1.13}$$

where the units of M are in Tesla.

### 1.4.2 Magnetic dipole moment

The elementary magnetic quantity of a solid with a volume V is the magnetic moment m:

$$\boldsymbol{m} = \boldsymbol{M} \boldsymbol{V} \tag{1.14}$$

where *M* is the magnetization. The magnetic moment is the quantity measured by a magnetometer. Its unit is typically given in emu, where 1 emu =  $10^{-3}$  A m<sup>2</sup>.

### 1.4.3 Demagnetization field

Any magnet will create an H field in the space around it and within its own volume. Figure 1.13 shows that inside a magnet the B field and the H field are oppositely directed. H is also oppositely directed to M inside the magnet, therefore  $H_d$  arises as the 'demagnetizing field'. The demagnetization field  $H_d$  relates to M through:

$$\boldsymbol{H}_{\boldsymbol{d}} = -\mathcal{N}\boldsymbol{M} \tag{1.15}$$

Here the tensor  $\mathcal{N}$  is the demagnetization factor. For a sphere,  $\mathcal{N} = 1/3$ .



Figure 1.13 Schematic of a magnetized object exhibiting the three magnetic vectors B, H and M in the absence of an external magnetic field. The magnetic field inside the object is called the demagnetization field  $H_d$ , whereas the field outside is called the stray field  $H_s$ . Inside the magnetized object, we have  $M = B - \mu_0 H_d$ .

# 1.4.4 External magnetic field

In this thesis, we often use the term the external magnetic field  $H_{ex}$ . This is the magnetic field acting on a sample that is produced by the **B** field of permanent magnets. The sample does not affect  $H_{ex}$ . When a sample is magnetized by  $H_{ex}$ , its magnetization **M** is given by:

$$\boldsymbol{M} = \chi \boldsymbol{H}_{ex} \tag{1.16}$$

Here  $\chi$  is the susceptibility of the sample, a dimensionless quantity. For paramagnets  $\chi > 0$  and for diamagnets  $\chi < 0$ . This equation is related to what is measured in a hysteresis loop by a magnetometer. The magnetization of a sample will increase until saturation,  $M_s$ , in an increasing H field. For simplicity, we denote external magnetic field as H.

### 1.4.5 Magnetic anisotropy

Magnetic anisotropy describes the dependence of magnetic properties on the direction of the applied magnetic field. Magnetic anisotropy of a material makes it energetically favorable to be magnetized along the so-called the easy axis, and least favorable along the hard axis. The

contribution to magnetic anisotropy can be traced to magnetocrystalline anisotropy, magnetostriction, shape anisotropy, surface anisotropy, and dipole-dipole interactions.<sup>62</sup> The first four types of anisotropy are intrinsic to magnetic materials. These can be quantitatively characterized by their corresponding anisotropy constant *K*. For bulk materials, magnetocrystalline and magnetostatic anisotropy dominates, whereas surface and shape anisotropy and dipolar interactions are significant in nanomaterials, such as thin films, nanoparticles and self-organized structures. Here we briefly discuss the anisotropies that are related to iron oxide nanoparticles. Dipolar interaction has been discussed earlier in Section 1.2.6.

Magnetocrystalline anisotropy results from the crystal structure of the materials. Magnetite and maghemite adopt a cubic crystal structure, for which the anisotropy energy can be expressed as:<sup>96</sup>

$$E_{a} = K_{1}V(\alpha_{1}^{2}\alpha_{2}^{2} + \alpha_{2}^{2}\alpha_{3}^{2} + \alpha_{3}^{2}\alpha_{1}^{2})$$
(1.17)

where  $K_1$  is the first order anisotropy constant, V is the particle volume,  $\alpha_1 = \sin\theta \cos\varphi$ ,  $\alpha_2 = \sin\theta \sin\varphi$  and  $\alpha_3 = \cos\theta$ ,  $\theta$  is the polar and  $\varphi$  the azimuthal angle. For a uniaxial structure like cones, the anisotropy energy is written as

$$E_a = K_1 V \sin^2 \theta \tag{1.18}$$

This expression describes two local energy minima at  $\theta = 0^{\circ}$  and 180°, and two maxima at  $\theta = 90^{\circ}$  and 270°.

Magnetostriction is caused by changes in the dimensions of the materials in response to the applied magnetic field. This anisotropy is often described by

$$E_{a} = -\frac{3}{2}\lambda_{s}\varepsilon S\cos^{2}\theta' \qquad (1.19)$$

where  $\lambda_s$  is the saturation magnetostriction coefficient, e is the strain value, S is the particle surface and  $\theta'$  is the angle between magnetization and the strain tensor axis. For magnetite, the magnetostriction coefficient  $\lambda_s$  is in the order of 10<sup>-6</sup>. Therefore, its contribution to the total anisotropy in MNP systems is negligible.

Shape anisotropy, as its name implies, results from the shape of the materials. A perfectly uniform spherical MNP has no shape anisotropy. For a non-spherical MNP, say ellipsoid for example, it is easier to magnetize along the long axis direction than other directions. This is because the demagnetization field of the MNP is different in easy and hard directions. For an ellipsoid, the shape anisotropy energy is written as

$$E_{a} = \frac{1}{2} \mu_{0} V M_{s}^{2} (N_{x} \cos^{2} \theta + N_{z} \sin^{2} \theta)$$
(1.20)

where  $N_x = N_y$  and  $N_z$  are the demagnetization factors along the polar and the equatorial axes, respectively.

Surface anisotropy is due to symmetry breaking (termination of the lattice) at the surface. This anisotropy is significant for ultrafine MNPs under low temperature. For MNPs with a diameter of 2 nm below 30 K,<sup>97</sup> the surface contribution dominates the magnetocrystalline anisotropy. For spherical MNPs with a diameter d, the surface contribution to effective magnetic anisotropy can be expressed as

$$K_{eff} = K_V + \frac{S}{V}K_S = K_V + \frac{6}{d}K_S$$
(1.21)

where  $K_v$  is the volume anisotropy consisting of magnetocrystalline, magnetostriction and shape anisotropy, *S* and *V* are the surface and the volume of the particle. In room (high) temperature, surface anisotropy in MNPs with size > 10 nm is negligible. In Chapter 5 we probe the magnetic anisotropy of individual MNPs and their self-organized superstructures by magnetometry and ferromagnetic resonance.

#### 1.4.6 Magnetometry

Magnetometers measure the strength and the direction of magnetic moments with respect to an external field. An inexpensive and versatile vibrating sample magnetometer (VSM) was developed by Foner in the 1950s.<sup>98</sup> The signal is acquired from an induced voltage caused by the sample vibrating perpendicular to the applied field, which can then be related to the magnetic moments of the sample. A sensitivity of  $10^{-5}$ – $10^{-6}$  emu can be obtained in the VSM measurements. A more sensitive magnetometer is the superconducting quantum interference device, or SQUID. A SQUID magnetometer can reach a limit of ~ $10^{-7}$  emu.<sup>99</sup> The SQUID magnetometer was invented by a team of scientists in the Ford Scientific Laboratories in the 1960s.<sup>100</sup> We use a state-of-the-art SQUID magnetometer MPMS (XL) from Quantum Design in this thesis to measure the magnetic moments of our MNPs. The common types of data acquired by magnetometry are the *M/H* curves or hysteresis loops under DC or AC field and the zero-field-cooled/field-cooled curves (ZFC/FC). The *M/H* curves yield information about saturation magnetization,  $M_s$ , and susceptibility d*M*/d*H* of a sample. From ZFC/FC curves one may extract the blocking temperature  $T_B$  and therefore the magnetic anisotropy of a sample according to Equation 1.9.<sup>101</sup>

### 1.4.7 Ferromagnetic resonance

Ferromagnetic resonance is the resonant absorption of electromagnetic radiation in ferromagnetic materials. Its physical origin lies in the presence of unpaired electrons. When an external magnetic

field is applied, the magnetic moments of electrons align parallel or antiparallel to the field. This alignment gives rise to separated energy levels due to the Zeeman effect:

$$\Delta E = hv = g\mu_B B \tag{1.22}$$

where g is the free electron g-value equal to 2.002,  $\mu_{\rm B}$  is the Bohr magneton and B is the applied magnetic field. The Zeeman energy splitting increases with increasing B. Absorption occurs when the energy difference matches the microwave radiation, which induces transitions between Zeeman levels to give rise to the spectroscopic signal. Recall in the previous section that each MNP is considered to possess a "macrospin". Each MNP possesses a total spin in the order of 10<sup>3</sup>, while an electron has a spin of 1/2. The FMR signals arise from an ensemble of MNPs and therefore the response is much broader than that of an electron. Equation 1.22 is strictly valid only for paramagnets. FMR requires that, to the Zeeman effect, we add the anisotropy and exchange fields, because these two affect the resonance condition.

The experimental configuration of FMR is similar to that used for EPR. Electron paramagnetic resonance is also known as electron magnetic resonance (EMR) or electron spin resonance (ESR). In a continuous wave EPR spectrometer, the sample is inserted into a cavity. The cavity is tuned until critically coupled, such that no microwave energy is detected. The DC magnetic field is swept with a constant microwave frequency to find the resonance field condition. Resonance absorption occurs when the energy difference between the two states caused by the Zeeman effect matches the microwave frequency. The signal is plotted as the first derivative of the absorption. While EPR probes organic radicals and transition metal ions with one or a few spins, the FMR response arises from ferromagnetic or ferrimagnetic materials that have a large number of spins (S >  $10^3$ ). In such systems, the FMR signal is broad, spanning a few hundred milli-Tesla and contains information

about magnetic anisotropy from different sources. In Chapter 5 we will further examine the FMR of magnetic nanoparticle systems.

# 1.5 Scope of the thesis

The scope of the thesis is pattern formation in ferrofluid systems that results from self-organization of magnetic nanoparticles. Formally, ferrofluid patterns are not stable—they collapse when the applied magnetic field is removed. This intrinsic instability makes studying self-organized structures in ferrofluids experimentally challenging. We provide solutions to this problem in the context of MNP self-organization with the techniques used in nanoparticle assembly.

Chapter 2 describes a simple method to trap ferrofluid patterns by evaporation-mediated selforganization of MNPs. Despite the simplicity of this method, defective patterns may be obtained if parameters are not controlled properly. Evaporation-derived mesoscale structures of MNPs were reported earlier by Pileni et al. and Lisjak et al.,<sup>102-104</sup> where ordered structures were only observed at the micron scale. We demonstrate that highly ordered patterns can be stabilized through properly controlled conditions. We systematically study the conditions affecting pattern formation in evaporative ferrofluids. Patterns are analyzed with MATLAB algorithm to extract characteristic parameters. In addition, we discover a correlation between the number of spikes in the trapped pattern and the saturation magnetization of MNPs used. Readers are recommended to watch the videos with the links embedded in the text.
Chapter 3 examines the role of the ligand oleic acid (OA) on pattern formation in the evaporative ferrofluid systems. We discover that controlling the amount of excess OA in evaporative MNP ferrofluids leads to formation of hexagonal, labyrinthine patterns and combinations of them. The progression of patterning from hexagonal to labyrinthine phases is observed for different MNP shapes and sizes, namely monodisperse spherical and cubic iron oxide nanoparticles. We use IR spectroscopy to probe the packing of OA in the trapped structures. In addition to stabilizing MNPs, the presence of excess ligands in ferrofluids can also impact self-organization process during evaporation. Interestingly, the emergence of the labyrinthine phase is linked to molecular organization of OA molecules that exhibits solid-like behaviours.

Chapter 4 turns to ferrofluid systems co-hosted with a crosslinking polymer additive. The goal of introducing the crosslinking polymer is to add a "reaction" component to the "diffusion" governed ferrofluid system. A surprising degree of morphogenesis emerges at various length scales as expressed in the solidified spike structures. These hierarchies of order can only be captured in the polymer-based ferrofluid system, which is strictly an out-of-equilibrium evaporation-reaction system. We suggest a way to take the "memory" of magnetic field-directed orientational anisotropy in spike structures and, by solid-state thermal transformation, transfer that anisotropy from the kinetically trapped magnetite nanocomposite template to a product of thermal transformation.

Chapter 5 probes the ferromagnetic resonance (FMR) response of the self-organized spike superstructures in the patterns derived from previous experiments. We compare the FMR response of three MNP systems—spherical, cubic and polydisperse MNPs. We report the first order

magnetocrystalline anisotropy constant for these MNPs from FMR linewidths in non-interacting MNP systems. We explore the FMR response of spike superstructures of interacting MNPs and uncover that the spike superstructures exhibit collective properties that their constituting MNPs do not possess.

Chapter 6 concludes the thesis and provides suggestions for future experiments.

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# **Chapter 2 Trapping the Rosensweig Pattern in Evaporative Ferrofluids**

## 2.1 Abstract

Ferrofluids consist of colloidal suspensions of superparamagnetic nanoparticles in non-volatile fluids. A spike pattern can be induced in ferrofluids in response to an applied magnetic field normal to the fluid surface. This normal field instability, or Rosensweig pattern, collapses when the field is removed. Here we provide a method to kinetically trap the Rosensweig patterns formed by oleic acid-decorated magnetite nanoparticles in ferrofluids. This is achieved by reformulating the fluid host with volatile alkane solvents. We then systematically map out the conditions affecting the order of the trapped patterns. The controlled variables include applied magnetic field, ferrofluid concentration, evaporation rate, solvent type and substrate. Differences among the patterns are quantified by a set of parameters including wavelength, number of spikes, size of spikes and Voronoi entropy. We suggest that the number of spikes in a ferrofluid trapped pattern is correlated with the saturation magnetization of the magnetic nanoparticles.

### 2.2 Introduction

Patterns in nature share extraordinary complexity and similarity over length scales that can extend from the individual element to the ecosystems comprising them.<sup>1</sup> It has long been a focus of inquiry why many physical and chemical systems should display similar patterns despite the underlying differences in their origin. For example, lamellar phases are expressed alike by magnetic garnets, by type I superconductors, by diblock copolymers, and by Langmuir films.<sup>2</sup> Their similar morphology apparently originates in the complex interplay of short-range repulsions, medium-range attractions and long-range repulsions.<sup>3</sup>

Ferrofluids consist of colloidal suspensions of magnetic nanoparticles (MNPs). They have been invoked as an artificial model system to study morphogenesis under static and dynamic conditions.<sup>4</sup> In this connection, ferrofluids exhibit a richness of structures and patterns that depend among other things on the applied magnetic field. Ferrofluid patterns include labyrinths, stripes, bubbles, rings, or foams, depending on properties like interfacial tension and the strength of the applied magnetic field.<sup>5</sup> In essence, pattern formation in ferrofluids is the outcome of self-organization of magnetic nanoparticles directed by magnetic fields. The relevant interactions are the short-range steric forces among the stabilizing ligands on MNPs, the medium-range van der Waals and dipole-dipole attractions between the parallelly aligned MNPs, and long-range repulsions between the aligned MNP chains.

The most familiar pattern formation response is often described in the framework of the Rosensweig instability,<sup>6</sup> where a hexagonal or square pattern of conical spikes can emerge from the ferrofluid surface in response to a sufficiently strong external magnetic field.<sup>7</sup> Experiments on

pattern formation in ferrofluids generally use formulations that suspend ligand-stabilized MNPs in a non-volatile fluid. The patterns that form collapse when the applied magnetic field is removed. This makes it difficult to establish links between the macroscopic patterns and the organization of MNPs within them. Until now, the research community has not had a materials system based on ferrofluids that can be used to link the intricate details of the relationship between field-directed, self-organized MNPs and the order-forming macro-patterns. We offer a pathway to bridge the nano-, meso- and macro-scales in this Chapter.

To explore the morphogenesis of macro-patterns from the nanoscale building block MNPs, it is desirable to trap the patterns and make them accessible to other characterization techniques, without the need for a sustained magnetic field. A clue to how to do this can be found in Pileni and coworkers who evaporated colloidal suspensions of Co nanoparticles in different magnetic fields to generate hexagonal and labyrinthine patterns at the microscale.<sup>8</sup> Elsewhere, Lisjak et al. evaporated water from colloidal suspensions of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles in a magnetic field to produce a random array of ~500 µm 3D spike structures.<sup>9</sup> They also showed that BaFe<sub>12</sub>O<sub>19</sub> nanoplatelets would assemble into 2D arrangements of flat film structures after evaporation under a magnetic field. Another example of a trapping experiment can be found in the work of Bian and McCarthy who used 1,5-cyclooctadiene or dicyclopentadiene as the fluid host.<sup>10</sup> They polymerized the diene-based ferrofluids in the presence of a magnetic field to trap the spike structures. Nonetheless, this approach yielded highly disordered spike topographies, from which little insight can be derived regarding the origin of the conical spike structures. Thus, there remains considerable incentive to trap the Rosensweig configuration to learn more about its morphogenesis.

In this Chapter, we demonstrate that evaporation of volatile alkane formulations of ferrofluids can trap patterns as stable solid structures. The patterns retain the symmetry of their fluid antecedents. To obtain reproducible, ordered patterns, we perform systematic studies of spike pattern formation in evaporative ferrofluids in the presence of an inhomogeneous magnetic field. We use MATLAB algorithm to process the hexagonal patterns of spikes and quantify the differences among the patterns with a set of parameters including wavelength, number of spikes, size of spikes and Voronoi entropy. We find that pattern formation is sensitive to a number of factors: applied magnetic field strength and gradient, ferrofluid concentration, evaporation rate, solvent type, and substrate interface. In addition, we suggest that the number of spikes in the Rosensweig pattern correlates to the saturation magnetization with the constituting MNPs.

## 2.3 Results and Discussion

#### 2.3.1 General pattern formation process

We first establish a standard experiment with well-defined conditions and then explore the impact of different variables on pattern formation. In the "standard" experiment, we start with a ferrofluid of 25 wt% magnetite nanoparticles in octane. It should be noted that magnetite nanoparticles were washed properly to remove excess ligands and the nanoparticles used were from the same batch of synthesis for the following results to be reproducible. A permanent disk magnet is used to create the field (**Figure 2.1A**). At the beginning of the experiment, the ferrofluid wets the circular polystyrene petri dish substrate. In the external magnetic field, the ferrofluid initially assumes a convex shape resembling a spherical cap, i.e. the contact angle of the fluid on the substrate decreases. We identify six stages of evaporation in **Figure 2.1B**. The starting **stage I** is shown in **Figure 2.1B-i** where we observe the top view of the quiescent ferrofluid with a circular perimeter. This perimeter is the three-phase contact line (liquid-solid-gas). The octane solvent is allowed to evaporate from the ferrofluid under atmospheric temperature and pressure. The magnetization (M)of the ferrofluid is the magnetization  $M_{\rm MNP}$  of MNPs diluted in the liquid host. This is given by  $M = M_{\rm MNP}/V$ , where V is the volume of the ferrofluid. The overall magnetization M of the ferrofluid increases because the fluid volume V decreases. When M reaches the critical magnetization  $M_c$  after ~10.5 min, the ferrofluid surface starts to deform yielding an outer ring, which is evident in the white reflection showing involutions and internal islands. The white reflections are due to light scattering from peaks and valleys of the emerging topographical elements. This onset pattern is denoted as stage II in Figure 2.1B-ii. The first spike then emerges near the center of the ferrofluid. It is followed by the evolution of more spikes. New spikes spawn in a central hexagonal pattern. At stage  $III \sim 17.5$  min, the ferrofluid surface is covered by spikes arranged hexagonally (see Figure 2.1B-iii). Subsequently, the circular outer boundary of the ferrofluid deforms into several larger spikes at stage IV in Figure 2.1B-iv. Up to this stage, we refer to the increase in the number of spikes as *spike spawning*. Meanwhile, smaller spikes arise from the contact line of the ferrofluid. Some spikes coalesce into other spikes already present at the outer perimeter. Others grow into larger spikes that populate the outer boundary. We conjecture that the fluid under the spikes migrates to the contact line from underneath to form unstable spikes. These are eventually devoured by the existing spikes or grow large and stable enough to fill in the lattice. At ~ 22 min, the lattice begins its next transformation: spike fission. Some large outer boundary spikes split into smaller spikes that participate in the rearrangement of the local positions of nearby spikes. We observe that spike fission can lead to defects. The number of spikes increases when spike fission occurs. By 27 min, the pattern becomes invariant in stage V: the number of spikes does not change (Figure 2.1B-v). With evaporation, the ferrofluid breaks into individual

spikes packed in a hexagonal array. Continued solvent evaporation is accompanied by the separation and shrinkage of the spikes. At the end **stage VI**, the final pattern in **Figure 2.1B-vi** is permanently trapped. It does not collapse when the magnetic field is removed. The whole process is captured in six key stages and can be viewed in the video in the link "Oct25\_140mT". Experiments at other initial conditions produce similar patterns that follow a similar evolution.



**Figure 2.1** Progression of ferrofluid pattern formation in a magnetic field leading to evaporative trapping of a hexagonal array of spikes. (A) Schematic representation of the experiment. (B) Macroscopic patterns induced in the ferrofluid (25 wt% Fe<sub>3</sub>O<sub>4</sub> NPs in octane) by a disk magnet.

The white ring that is visible in the figure is due to the circular ring light source that provides top illumination. The scale bar is 2 mm. Snapshots of the time evolution of the patterns with gradual changing level of solvent loss at (i) t = 0 min, quiescent liquid film; (ii) t = 10.5 min, spikes emerge from the surface; (iii) t = 17.5 min, spikes in a hexagonal lattice, (iv) t = 22 min, fluid boundary deforms into spikes; (v) t = 27 min, invariant hexagonal lattice of spikes; (vi) t = 32 min, the trapped hexagonal pattern.

Conventional non-volatile ferrofluids are prepared with a fixed magnetic nanoparticle concentration that is designed to yield a Rosensweig pattern when a sufficient magnetic field is applied.<sup>11</sup> In our systems, we use the volatile solvent host to introduce time-dependent evaporation among several related variables to probe pattern formation: the fluid volume decreases over time with a concomitant increase in ferrofluid magnetization. Evaporation induces a surface tension gradient that changes across the fluid surface.<sup>12</sup> Surface tension is a stabilizing factor for the fluid surface to resist deformation; this time- and space- varying surface tension governs the evolution of patterns under a constant magnetic field. In the following sections, we will examine a number of conditions that may impact surface tension and therefore pattern formation. These conditions are magnetic field and field gradient, concentration, evaporation rate, solvent carbon number and substrate.

#### 2.3.2 Effect of the magnetic field on pattern formation

In this section, we examine the effect of different inhomogeneous magnetic fields on pattern formation in evaporative ferrofluids. Homogeneous magnetic fields produced by Helmholtz coils are widely used to study Rosensweig instabilities. This is because the field strength is tunable through the control of the current. An inhomogeneous field created by a permanent magnet is of interest because it introduces the variable of the magnetic field gradient dH/dz, where z is the direction orthogonal to the plane of the unperturbed fluid. We discover that a large field gradient can suppress the Rosensweig instability pattern. For example, we observe that a ferrofluid comprising 33 wt% MNPs can spike in a field of 140 mT but can be forced to flatten by increasing the field to 250 mT. The field strength is easily adjusted by raising and lowering the magnet. We then set out to investigate the effect of field gradient in the inhomogeneous magnetic field on ferrofluid patterning.

We first vary the magnetic field applied to a ferrofluid of 25 wt% MNPs in octane which has an initial magnetization below  $M_c$ . Five magnetic fields in the range 250 mT to 80 mT were generated by varying the distance between the permanent magnet and the samples over the range 5–15 mm. Decreasing the distance produces a stronger field strength at the sample and a larger field gradient in the sample plane (see Section 2.5.3 for details). The closest approach is limited to 5 mm to avoid field distortion caused by the geometry of the disk magnet. A stronger magnetic field strength with a concomitant larger field gradient acts on the sample film. Accordingly, five samples of the same ferrofluids were allowed to evaporate in these five magnetic fields. The pattern formation process can be viewed in the videos by the following links: "Oct25\_80mT", "Oct25\_100mT", and "Oct25\_250mT".

The ferrofluids used in the five samples have identical compositions at the outset. Despite the common starting point, we observe that the onset time for patterning depends on the external field *H*: the higher is *H*, the longer is the time required for the onset of the instability. The onset time is 2' 39", 4' 35", 4' 45", 6' 58", and 8' 30" for the applied magnetic field of 80 mT, 100 mT, 140 mT,

190 mT and 250 mT, respectively. Patterning is governed by M, which must reach the critical magnetization  $M_c$ . At constant temperature and pressure, and assuming that the rate of solvent evaporation is independent of the applied field H, the magnetization M increases at the same rate for each sample. The magnetization of our ferrofluids was determined independently by SQUID magnetometry (Figure S2.3) and the conventional relationship,

$$\boldsymbol{M}(\boldsymbol{H}) = \boldsymbol{\chi} \boldsymbol{H} / \boldsymbol{V} \tag{2.1}$$

where  $\chi$  is the magnetic susceptibility and H is the applied magnetic field strength. The magnetization  $M_{\text{MNP}}$  increases with the strength of the applied magnetic field H until it reaches the saturation magnetization  $M_{\text{s}}$ . For instance, the initial magnetization M of the ferrofluid (25 wt% MNPs in octane) in the 250 mT field is roughly twice as large as that in an 80 mT field. The ferrofluid exposed to the highest field of 250 mT has the largest initial magnetization M of the five samples, yet it is the last to reach the  $M_c$  required for patterning. This suggests that the  $M_c$  is larger for a sample exposed to a higher H field, i.e.  $M_c$  depends on the applied H field. This contrasts with what would be predicted from Rosensweig's linear analysis, where the critical magnetization  $M_c$  is given by:

$$M_c^2 = \frac{2}{\mu_0} \left( 1 + \frac{\mu_0}{\mu} \right) \sqrt{\rho g \gamma}$$
(2.2)

Here  $\mu_0$  is permeability of vacuum,  $\mu$  is the permeability of the ferrofluid,  $\rho$  is the density, *g* is gravitational acceleration, and  $\gamma$  is the interfacial tension. In this framework,  $M_c$  is clearly independent of the magnetic field strength. Note that this expression holds only when the applied *H* field is uniform. In contrast, the magnetic field produced by a permanent magnet has a larger field gradient over the volume where the sample is placed. The field gradient exerts a gradient force  $d(\mu_0 HMV)/dz$  that is much stronger than the gravity term  $\rho g V$ . Vieu and Walter provide an expression for the Rosensweig instability in a non-uniform magnetic field.<sup>13</sup> With some

adjustments to their theory, we can link the adjustable parameters, solvent surface tension and field gradient, to our experiments. In line with Vieu and Walter,<sup>13</sup> we therefore write the critical magnetization  $M_c$  and the peak-to-peak wavelength  $\lambda$  of the pattern as

$$M_{c}^{2} = \frac{2}{\mu_{0}} \left( 1 + \frac{\mu_{0}}{\mu} \right) \sqrt{\frac{d}{dz} (\mu_{0} H M) \gamma}$$
(2.3)

$$\lambda = 2\pi \sqrt{\frac{\gamma}{\frac{d}{dz}(\mu_0 HM)}}$$
(2.4)

In these expressions, H is the applied magnetic field and M is the magnetization of the ferrofluid. From Equation 2.3, we can see that  $M_c$  increases with the field gradient term  $d(\mu_0 HM)/dz$ . This is in accordance with the longer onset time for a larger field.

The trapped patterns under these five magnetic fields are shown in **Figure 2.2A**. We interpret the patterns with a set of parameters as listed in **Table 2.1**. The number of spikes *N* decreases with decreasing *H* field/field gradient. Simultaneously, the size of spikes, characterized by their average height and diameter, increases. This is evident in **Figure 2.2C**. The wavelength  $\lambda$  of the pattern is measured by the peak-to-peak distances between the spikes (see Section 2.6.1 for detail). The wavelength  $\lambda$  increases with decreasing *H* field/field gradient, as predicted by Equation 2.4. The trend of parameters of the patterns is shown in **Figure 2.2C**.



**Figure 2.2** Effect of magnetic field on parameters of pattern formation in 25 wt% octane ferrofluids. (A) Trapped patterns in different applied magnetic fields. Patterns were bit-mapped for clarity. (B) Voronoi diagrams of the corresponding patterns. Hexagons are colored in green to indicate order of the pattern. (C) Plot of number of spikes, wavelength, diameter and height versus the applied magnetic field. With a decrease in the applied field, the number of spikes decreases, and the wavelength of the pattern increases with a larger standard deviation. Accordingly, the diameter and height of spikes increase.

A Voronoi diagram can be used to quantify the degree of order in a pattern.<sup>14</sup> We then constructed the Voronoi diagrams of patterns generated at different magnetic field strengths. The diagrams were made by determining the spatial coordinates of the spikes, from which the probabilities  $P_n$  of the Voronoi polygons with n sides were obtained (details can be found in Section 2.6.1).<sup>15, 16</sup> **Figure 2.2B** shows the Voronoi diagrams for the five patterns with respect to the different magnetic fields. The hexagons in the Voronoi diagrams are colored in green to help visualize order in the pattern. The Voronoi entropy  $S_{vor} = -\sum P_n \ln P_n$  was then calculated. The more ordered the pattern, the smaller the Voronoi entropy. In **Figure 2.2B**, the pattern obtained under 100 mT field is visually most defected (fewer green hexagons) and has the highest  $S_{vor}$  of 1.42. In other patterns, the central hexagonal lattice is ordered, and defects occur in the form of square arrays near the circular boundary which inscribes the hexagonal lattice. We can also use the standard deviation  $\sigma$  of the wavelength  $\lambda$  to estimate order, because the peak-to-peak distances in ordered patterns should be more convergent to the mean of the dataset and therefore have a smaller  $\sigma$ . We observe that an increase in the *H* field/field gradient yields a smaller  $\sigma$  for the pattern, as shown in **Table 2.1** and the error bar of the green dots in **Figure 2.2C**.

**Table 2.1** Parameters used to describe the patterns that develop as functions of applied magnetic fields. *N* is number of spikes, *d* is diameter of spikes, *h* is height of spikes,  $\lambda$  is wavelength,  $\sigma$  is the standard deviation of wavelength and *S*<sub>vor</sub> is the Voronoi entropy. Units: mm (other than  $\sigma$  and S<sub>vor</sub>).

Applied Field (mT)	250	190	140	100	80
h	1.05	1.36	1.51	1.96	2.39
d	0.51	0.66	0.75	0.94	1.17
Ν	228	112	75	42	26
λ	0.89	1.11	1.29	1.64	1.99
σ	0.088	0.104	0.109	0.195	0.247
Svor	1.00	1.19	1.07	1.42	1.22

#### 2.3.3 Effect of MNP concentration on pattern formation

The concentration of ferrofluids at 25 wt% is much higher than that of colloidal suspensions of nanoparticles used for self-assembly in other systems, which is typically < 1 wt%. We are then motivated to investigate if lower nanoparticle concentrations might improve ordering (reduce defects) in the trapped macro-patterns. In this section, we vary the concentration of ferrofluids while fixing the quantity of MNPs to 33 mg and the applied magnetic field to 140 mT.

We begin with a stock ferrofluid of 33 wt% MNPs. For lower concentrations, octane was added to obtain concentrations of 20 wt%, 15 wt%, 10 wt%, 5.0 wt% and 1.0 wt% MNPs. Because the mass of MNPs is fixed at 33 mg, the starting ferrofluid mass with different concentrations increases from 100 mg to 3.30 g accordingly. Except for the 1.0 wt% ferrofluid, the pattern formation process for these samples can be viewed as videos by following the links: "Oct33\_140mT", "Oct20\_140mT", "Oct15\_140mT", "Oct10\_140mT", "Oct5\_140mT".

For a 33 wt% ferrofluid composition, we observe spike formation immediately as the field is applied. This response indicates that the initial magnetization M prior to evaporation exceeds  $M_c$ . No initial pattern onset occurs in ferrofluids with nanoparticle concentration at 25 wt% or less. A lower concentration results in an increase in the evaporation time of the ferrofluids before the pattern onset, i.e. the time in quiescent **stage I** is longer. After pattern onset, it takes ~20 minutes for samples to dry completely.

**Figure 2.3A** shows the resulting patterns and **Figure 2.3B** collects their corresponding Voronoi diagrams. Minute differences can only be discernable from the pattern parameters. The wavelengths of the seven patterns derived from ferrofluids of different compositions increase from 1.28 mm to 1.38 mm as the concentration decreases. Spike size remains consistent with the change in ferrofluid concentration. The size is characterized by the average height and diameter of the spikes, which are 1.50 mm ( $\sigma \sim 2.4\%$ ) and 0.73 mm ( $\sigma \sim 3.3\%$ ), respectively.



**Figure 2.3** Effect of MNP concentration on pattern formation in octane ferrofluids at fixed applied magnetic field. (A) Trapped hexagonal patterns from different initial MNP concentrations. Patterns are bit-mapped for clarity. (B) Voronoi diagrams of the corresponding patterns. Hexagons are colored in green to indicate order of the pattern. (C) Plot of number of spikes, wavelength, height and diameter versus MNP concentration. The wavelength is ~1.29 mm. The height and diameter of spikes are ~1.50 mm and ~0.73 mm, respectively.

By evaporation, a ferrofluid starting at a lower concentration of say 1.0 wt% MNPs will eventually approach and become equal to that of a fluid starting with a concentration of 5.0 wt%, and up to 10 wt%, and to eventually even higher concentrations. Trivially, lower MNP concentrations require more solvent to evaporate at **stage I** before pattern onset; but what happens at **stage I** does not appear to have a significant impact on the order in the trapped patterns. This is supported by the fact that the Voronoi entropy and standard deviation do not show a concentration dependence. We now take a closer look at some of the other variables.



**Figure 2.4** Optical micrograph near the outer perimeter of a spike pattern derived from 25 wt% MNP ferrofluid in a magnetic field of 140 mT. The lower right corner is the edge of the pattern. Outside the pattern, one observes thin layers of MNP deposits on the substrate. A radial flow field pattern is visible from the upper left to lower right corner in this image, indicating the flow direction of the ferrofluid. These deposits reduce the quantity of MNPs for spikes.

We observe that the number of spikes N decreases from 75 to 69 as the MNP concentration decreases from 33 wt% to 1 wt% MNPs, except for the 10 wt% MNP sample. We attribute the

decrease in the number of spikes to the loss of MNPs by adsorption onto the substrate at **Stage I**. When the ferrofluid is deposited on the polystyrene substrate under ambient conditions, it will undergo the processes of wetting and drying spontaneously. The pool of ferrofluid spreads and wets, undergoes contact line retraction, experiences flow fields within the fluid, and mass transportation within it during drying. The contact line retraction at **Stage I** leaves behind light brown deposits of MNPs. **Figure 2.4** shows an optical micrograph of the thin layer near the outer edge of the pattern. The effects of the radial flow field are evident in the micrograph. Nanoparticle sedimentation therefore reduces the quantity of MNPs available for spike formation.

Among all patterns in **Figure 2.3**, the pattern from the 10 wt% MNP ferrofluid has an unusually high number of spikes and a penta-hepta defect in the central lattice. When examining the video "Oct10\_140mT", we note that an artifact—a piece of white printing paper that was used to enhance the contrast for image acquisition—was unintentionally left on the magnet and slipped away half-way through evaporation. One would think a piece of printing paper (thickness ~0.240 mm), which is non-magnetic, should not affect the pattern formation. The reason why this unintentional artifact leads to the anomaly in the trapped pattern may be due to some influence on the pattern of the diamagnetic susceptibility of the printing paper. We can see that the patterning is sensitive to small changes in the experimental configuration.

In this study, we have limited our samples up to a maximum 33 wt% MNP loading in the alkane. Beyond this loading, the ferrofluid generates a Rosensweig pattern instantaneously because its initial magnetization is above  $M_c$ . For instance, under a 140 mT magnetic field, a ferrofluid with 50 wt% MNPs instantly yields a pattern, but the individual spikes vary in size and the resulting pattern is highly defected.

MNP conc.	33%	25%	20%	15%	10%	5.0%	1.0%
h	1.50	1.51	1.48	1.47	1.45	1.53	1.56
d	0.69	0.73	0.75	0.72	0.72	0.76	0.75
N	75	75	72	71	77	70	69
λ	1.28	1.29	1.30	1.31	1.30	1.36	1.38
σ	0.112	0.109	0.117	0.111	0.121	0.107	0.0875
Svor	0.91	1.07	1.09	1.14	1.06	1.06	0.93

**Table 2.2** Parameters associated with trapped patterns from ferrofluids with different initial MNP concentrations. Units: mm (other than  $\sigma$  and *Svor*).

#### 2.3.4 Effect of evaporation rate on pattern formation

Control of the convective flow and evaporation at the sample surface can impact patterning. In this section, we vary the evaporation rate for octane ferrofluids at starting concentrations of 25 wt% MNPs and a fixed applied field of 140 mT. The evaporation rate of octane was controlled by partially covering the polystyrene petri dish holding the ferrofluid (see Section 2.5.2 for details). We produce two samples that we refer to as "Slow" and "Moderate", to distinguish their differently reduced evaporation rates. When evaporation is reduced in this manner, we observe that the trapped patterns have a lower defect density. This is supported by the fact that both the Voronoi entropy and standard deviation are smaller than those of the "Standard" sample which yielded the

pattern in **Figure 2.1**. To accelerate the evaporation rate, a hot air flow was directed across the surface of the sample. The trapped pattern in this case is referred to as "Fast". The findings are collected in **Figure 2.5** where they are compared with the "Standard" sample. Faster evaporation results in an increase in the Voronoi entropy of the pattern and a larger standard deviation (**Figure 2.5C**).



**Figure 2.5** Effect of evaporation rate on the pattern formation in octane-based ferrofluids. (A) Comparison of the trapped patterns obtained according to the evaporation rate. The sample names literally denote the rate of the process. (B) The corresponding Voronoi diagrams of the patterns. The Voronoi entropy decreases as the evaporation rate decreases. (C) Plot of number of spikes, wavelength, diameter and height versus the evaporation rate. Both an increase and a decrease in evaporation rate result in a larger number of spikes. The wavelength decreases with an increase in the evaporation rate.

Interestingly, both an increase and a decrease in the evaporation rate results in an increase in the number of spikes. For fast evaporation, the increase in spike numbers comes mainly from the fission of the larger spikes at the perimeter (see video "Oct25\_fast"). Timonen et al. pointed out that the criterion for spike fission is given by the critical wavelength  $\lambda_c$ :<sup>4</sup>

$$\lambda_{\rm c} = 2\pi \sqrt{\frac{\gamma}{\frac{d}{dz}(\mu_0 HM)}} \tag{2.5}$$

Spikes undergo fission when the diameter of the spike is larger than  $\lambda_c$ , which depends on surface tension and field gradient. This critical wavelength takes the same form as Equation 2.4, which means that any spikes larger than the wavelength of the pattern will fission. In the fast evaporation sample, larger spikes form at the edge in **stage IV** and by our criterion are susceptible to fission. In the case of slower evaporation, we observe that smaller spikes form at the edge. No spike fission occurs, because the spikes are smaller than  $\lambda_c$ .

#### Why does wavelength decrease with faster evaporation?

The wavelength of the permanent patterns decreases with faster evaporation (**Table 2.3**). Tracing back to the initial pattern onset in the **stage II** of evaporation, the wavelength is indeed smaller for faster evaporation (see snapshots in supporting **Figure S2.4**). Note that the starting ferrofluid and the applied magnetic field are identical for the four samples studied under the different evaporation rates. Equation 2.4 implies that a smaller wavelength corresponds to a smaller surface tension of the ferrofluid. Therefore, faster evaporation leads to a lower surface tension in the ferrofluid.

It is well-established in the theory of drying of colloidal fluids that solvent will evaporate faster at the contact line than at the top of the surface.<sup>17</sup> This unbalanced evaporation results in a

concentration gradient within the evaporating fluids, which leads to a surface tension gradient across the fluid surface. The resulting surface tension at the top surface is lower than that at the contact line. During fast evaporation, we suggest that the associated temperature change dominates at short timescales. The hot air drives solvent molecules to evaporate by heating and removing solvent vapor from the fluid surface. The input of heat compensates for the latent heat of evaporation that would tend to cool the surface. Surface tension is lowered with an increase in temperature. Therefore, faster evaporation causes a lower surface tension and therefore a smaller wavelength. In the slow evaporation process, the temperature variation is insignificant over the long timescale. When evaporation is slower, the concentration gradient is smaller, and the surface tension gradient is smaller. Under this condition, the surface tension at the top of the ferrofluid is higher than that experienced for faster evaporation. The higher surface tension results in a larger wavelength in the trapped pattern.

**Table 2.3** Parameters of the trapped patterns obtained from octane ferrofluids of 25 wt% MNP at different evaporation rate. Units: mm (other than  $\sigma$  and  $S_{vor}$ ).

Evaporation rate	Slow	Moderate	Standard	Fast
h	1.31	1.40	1.51	1.46
d	0.687	0.727	0.738	0.809
Ν	90	80	75	92
λ	1.38	1.34	1.29	1.20
σ	0.108	0.101	0.109	0.144
Svor	0.95	0.97	1.07	1.18

#### 2.3.5 Effect of solvent on pattern formation

Having examined the effects of evaporation rate in pattern formation, we now investigate the impact of fluid host alkane carbon number on ferrofluid patterns. We selected the normal alkanes, hexane (C<sub>6</sub>H<sub>14</sub>), heptane (C<sub>7</sub>H<sub>16</sub>), nonane (C<sub>9</sub>H<sub>20</sub>) and decane (C<sub>10</sub>H<sub>22</sub>) for study. **Table 2.4** lists some relevant physical properties of these alkanes as a function of their carbon number. The rate of evaporation is inversely related to the vapor pressure of the alkane. The lower the vapor pressure, the faster the evaporation rate. The starting MNP concentration of ferrofluids in each case is 25 wt%. The pattern formation process can be viewed via the video links "Hex25", "Hep25", "Oct25", "Non25" and "Dec25".

When a magnetic field of 140 mT is first applied, the hexane based ferrofluid produces spikes instantaneously, whereas all other alkane ferrofluids remain initially quiescent, unaffected by the field. This suggests that hexane ferrofluids have a lower  $M_c$  compared to the others. This is in accordance with what Equation 2.3 predicts: ferrofluids with a smaller  $\gamma$  will have a lower  $M_c$ .

A 11	Viscosity	Density	Vapor Pressure	Surface tension (liquid/air)
Alkane	mPa∙s	g/cm <sup>3</sup>	(kPa@20°C)	$(mN \cdot m^{-1})$
n-hexane	0.297	0.655	20.5	18.43
n-heptane	0.418	0.684	5.33	20.14
n-octane	0.546	0.703	1.47	21.60
n-nonane	0.713	0.718	0.341	22.85
n-decane	0.920	0.730	0.195	23.83

Table 2.4 Selected physical properties of alkane solvents. Data are obtained from reference (18).

The surface tension  $\gamma$  increases from 18.43 to 23.83 mN·m<sup>-1</sup> for hexane to decane. The permanent patterns derived in these alkanes are shown in **Figure 2.6A** along with their Voronoi diagrams in **Figure 2.6B**. According to Equation 2.4, we expect the wavelength of the patterns to increase with  $\gamma$ , and this is what we observe. This is evident in **Figure 2.6C**. The degree of order of the hexagonal lattices increases from hexane to decane, as indicated by the decrease in the Voronoi entropy from 1.16 to 0.92 and standard deviation from 0.142 to 0.081 (**Table 2.5**).



**Figure 2.6** Effect of solvent on the pattern formation in alkane ferrofluids. (A) Comparison of the trapped patterns obtained from alkane solvents of different carbon number. Patterns are bit-mapped from the original full-color images. (B) The corresponding Voronoi diagrams of the patterns in (A), showing that the Voronoi entropy decreases with an increase in carbon number of the alkane solvent. (C) Plot of the number of spikes, wavelength, diameter and height versus the solvent type.

Solvent	Hexane	Heptane	Octane	Nonane	Decane
h	1.45	1.50	1.51	1.49	1.40
d	0.81	0.82	0.78	0.82	0.77
N	108	85	75	82	86
λ	1.19	1.29(3)	1.29(4)	1.36	1.37 <sup>a</sup>
σ	0.142	0.115	0.109	0.098	0.081 <sup>a</sup>
Svor	1.16	1.08	1.07	0.934	0.922 <sup>a</sup>

**Table 2.5** Parameters of the trapped patterns obtained from ferrofluids in different alkane solvents under an applied magnetic field of 140 mT. Units: mm (other than  $\sigma$  and  $S_{vor}$ ).

<sup>a</sup>Note that we have omitted the smaller spikes at the periphery in the decane sample for calculation, otherwise the defect in the boundary obscures the actual representative value in the central lattice.

Surprisingly, the number of spikes decreases from hexane to heptane to octane, and then increases from octane to nonane to decane. We find the answer in the videos. The number of spikes is governed by two dynamic processes during pattern formation: spike spawning and spike fission. At **stage IV** of evaporation, the number of spikes is 87, 70, 71, 82 and 87 for ferrofluids in hexane through decane, respectively (consult supporting **Figure S2.5**). At **stage V**, larger spikes at the perimeter undergo fission in hexane, heptane and octane ferrofluids. Fission increases the number of spikes to 108, 85 and 75 for hexane, heptane and octane ferrofluids. Instead, one small spike at the perimeter coalesces with another spike in the decane sample, leading to the decrease of number from 87 to 86. The number of spikes in nonane ferrofluids remains at 82. In a nutshell, using alkanes other than octane results in an increase in the number of spikes, which is similar to what
is observed in the study of controlled evaporation rate in octane ferrofluids, where changing the evaporation rate results in an increase in the number of spikes.

#### 2.3.6 Effect of the choice of substrate surface on pattern formation

Let us now briefly consider possible effects of the substrate surface energy on ferrofluid patterning. The substrate surface interacts with the ferrofluid in contact with it, prior to, and during evaporation in an applied magnetic field. This raises the question, how might the pattern produced by the ferrofluid depend on the substrate surface energy? This is a complex problem, particularly given our use of an inhomogeneous magnetic field and the high concentrations of MNPs in our experiments. In fact, little at all is known about the effects of a magnetic field on interfacial tension. Interfacial tensions are usually assumed to be independent of the magnetic field.<sup>19</sup> We begin therefore, with a cursory examination of wetting of ferrofluid on different substrates with/without an applied magnetic field.

In our experiments described so far, we have used a polystyrene petri dish as the substrate vessel to excite patterns from our ferrofluid formulations. In this section, we extend to other substrates: borosilicate glass, Teflon<sup>®</sup> (polytetrafluoroethylene, or PTFE) and silicon (see Section 2.5.2 for sources of the substrates). In zero magnetic field, the hydrophobic ferrofluids wet the substrates differently. The octane ferrofluid wets the polystyrene petri dish completely, i.e. the contact angle is zero. In contrast, the contact angles  $\theta$  of octane ferrofluids are estimated to be  $0^{\circ} < \theta < 90^{\circ}$  on the silicon, glass and Teflon substrates. We were not able to measure the apparent contact angle at this stage because of the volatile solvent we used. In zero field, the wetting behavior of our

ferrofluids is primarily determined by the interaction between the ferrofluid surface and the substrate surface.

#### "Magnetowetting": wetting of ferrofluids on the substrates in an applied field

When the magnetic field is applied, the ferrofluids respond by a fluid flow that results in contraction of the mass of fluid away from its original outer physical boundary and formation of a large convex fluid "droplet" geometry that is similar in shape, independent of the type of substrate (see supporting **Figure S2.6** for their snapshots at time zero). Latikka and coworkers pointed out that this change in the ferrofluid shape in an applied magnetic field is related to the volume, magnetization and internal magnetic field of the ferrofluid.<sup>19</sup> This should be considered separately from the wetting interface of ferrofluid with the solid substrate. Simply stated, an external field can distort the ferrofluid and the apparent contact angle without affecting any intrinsic wetting properties of the ferrofluid. The "magnetowetting" of thick ferrofluid films and its impact on the Rosensweig instability remain elusive.

Despite these challenges, we chose to examine the response of a constant volume of the standard ferrofluid formulation of 25 wt% MNP in octane to a 140 mT field as a function of the different substrates. The pattern formation processes can be viewed by following the links to the videos "Oct25\_silicon", "Oct25\_glass" and "Oct25\_teflon". The trapped patterns and their corresponding Voronoi diagram are collected in **Figure 2.7**.

When the magnetic field is applied to the ferrofluid on the silicon substrate, eight spikes emerge instantaneously. This suggests that  $M_c$  for the silicon sample is lowered with respect to the control

sample on the polystyrene substrate. Video "Oct25\_silicon" reveals that six of the spikes arrange into a pentagon, and that subsequent spikes evolve into a hepta-penta defect near the center of the pattern. For the silicon sample, 70 spikes form by **stage VI** of the evaporation process. Spike fission occurs near 12 min, leading to the final 73 spikes. This number is fixed in the trapped pattern when evaporation ends after ~20 min. Interestingly, the total number of spikes that appears with the silicon substrate is close to that of 75 with the polystyrene substrate. Other parameters of the pattern on silicon, including the size of spikes, the wavelength and the defect density of the pattern, differ from those resulting from the use of the polystyrene substrate.



**Figure 2.7** Effect of the substrate on the pattern formation in octane ferrofluids of 25 wt% MNPs at a magnetic field of 140 mT. (A) Comparison of the trapped patterns obtained in different substrates. Patterns are bit-mapped for clarity. (B) The corresponding Voronoi diagrams of the patterns. Based on the Voronoi entropy, the glass and Teflon substrates yield more ordered patterns, whereas the silicon sample exhibits the most defects.

Patterning on the glass and Teflon substrates progresses similarly: the surfaces show spikes after  $\sim$ 3 min; spike fission occurs at  $\sim$ 12 min and the solvent evaporation ends after  $\sim$ 20 min when the pattern becomes fixed. The number of spikes prior to spike fission is found to be 80 for the glass substrate and 96 for the Teflon substrate. Following spike fission, the number of spikes on glass increases to 91 and to 99 for Teflon. Compared with the polystyrene substrate, the size of the spikes is smaller (**Table 2.6**). The wavelength for the two samples is also smaller than that measured with the polystyrene substrate. Moreover, a comparison of the two patterns shows that they are more ordered than that on the polystyrene substrate.

**Table 2.6** Parameters of the trapped patterns obtained from different substrates.  $\chi$  is the magnetic susceptibility (dimensionless),  $E_s$  is the surface energy of the substrate (unit: mJ m<sup>-2</sup>). Units for *h* and *d* are in mm.

Substrate	Silicon	Polystyrene	Polystyrene Glass	
$\chi^{a}$	$-0.325 \times 10^{-5}$	$-0.75 \times 10^{-5}$	$-1.063 \times 10^{-5}$	$-1.025 \times 10^{-5}$
$E_{ m s}$	39-52 <sup>b</sup>	29–43 <sup>20</sup>	60–83 <sup>21</sup>	$20^{22}$
h	1.60	1.51	1.41	1.41
d	0.794	0.738	0.753	0.673
N	73	75	91	99
λ	1.28	1.29	1.20	1.13
σ	0.131	0.109	0.113	0.114
$S_{ m vor}$	1.16	1.07	0.953	1.03

<sup>a</sup>The susceptibility data are obtained from reference (23). Minus sign means these substrates are diamagnetic. Air is paramagnetic with  $\chi$  of 3.6 × 10<sup>-7</sup>.

<sup>b</sup>The surface of silicon spontaneously and rapidly oxidizes in air at room temperature. The surface energy should correspond to that of silicon oxide, obtained from reference (*24*).

Examining the entries in **Table 2.6** we find no obvious link between surface energy and the number of spikes N or the spike pattern wavelength  $\lambda$ . Nevertheless, the column under Teflon deserves some scrutiny. Teflon has significantly lower surface energy than the other entries. We also observe that it yields the largest number of spikes that are comparatively well ordered. The spike base diameters in this instance are the lowest among the samples, suggesting that MNP mass that might have fed the base was diverted by fluid flow across the surface to nourish additional spike formation during patterning. The spike height from the Teflon sample is, on average, the same as that recorded from the pattern on the glass substrate. In the latter case though, there are 8 fewer spikes compared with Teflon and the spike diameters on glass are substantially larger. Again, this comparative observation suggests that mass has gone into building the spike base on glass, but not into height. Consistent with the increase in spike count on Teflon, the wavelength for the pattern is the smallest.

Clearly, more work needs to be done to examine the effect, if any, of the surface energy of the substrate on macroscopic patterning. Substrate surfaces need to be well characterized in terms of surface energy (advancing and receding contact angle measurements), surface defects and topography (atomic force microscopy), local humidity, and surface contaminants (x-ray photoelectron spectroscopy). Because oleic acid can chelate to oxide surfaces other than magnetite, loss of ligand from the MNPs might alter the interfacial tension and the aggregation behavior of the nanoparticles. Theis-Bröhl et al. showed that magnetite nanoparticles self-assemble into a monolayer on the silicon substrate in ferrofluids.<sup>25</sup> This layer of magnetite nanoparticles alters the wetting behavior of the ferrofluids. This may also affect patterning in our silicon sample.

## 2.3.7 Practical application of the study

We make the phenomenological observation that the pattern parameter N for the number of spikes is proportional to the saturation magnetization of MNPs, provided that the pattern is obtained with a field strong enough to saturate the MNPs, and other conditions are kept constant. This pattern parameter N can be used as a simple indicator to estimate  $M_s$  of MNPs when access to expensive magnetometry is limited. From **Table 2.6** we note that 75 spikes are produced from a 25 wt% MNP formulation in octane in a field of 140 mT. The sample has a saturation magnetization  $M_s$  of 73.3 emu/g (**Figure S2.3**). We compared this spike number with that from a batch of maghemite MNPs that had been obtained by long exposure of magnetite to air (oxidation of the magnetite to maghemite). Oxidation is evident in the brown hue of maghemite MNPs as opposed to the saturated black pigmentation of the magnetite.<sup>26</sup> We can therefore estimate  $M_s$  of the maghemite MNPs to be  $73.3 \times 0.80 \cong 58.6$  emu/g. We then acquired a pattern from a 25 wt% ferrofluid of the maghemite MNPs produced in a 140 mT field. This is shown in **Figure 2.8**. We counted N = 60spikes for this sample, a number that is very close to what we predict for the  $M_s$  value.



**Figure 2.8** The trapped hexagonal pattern derived from a 25 wt% ferrofluid of maghemite MNPs in a magnetic field of 140 mT. The number of spikes in this pattern is 60.

## 2.4 Conclusions

By now, we have demonstrated how to trap Rosensweig pattern formation in evaporative ferrofluids. We show that parameters associated with the patterns are sensitive to a number of factors including the magnetization of the nanoparticles, ferrofluid concentration, magnetic field strength and gradient, solvent type, and substrate interface. We also suggest that the ferrofluid patterning can be used to estimate saturation magnetization of the comprising magnetic nanoparticles.

# 2.5 Materials and Methods

## 2.5.1 Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by coprecipitation

The synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was adapted from Massart.<sup>27</sup> Water was purified by a Millipore Milli-Q system (0.0003 mS/cm) and degassed by purging with argon for 30 min prior to use. In a typical synthesis, FeCl<sub>3</sub> (3.24 g, 20 mmol, 97% Sigma-Aldrich) and FeCl<sub>2</sub> (2.03 g, 16 mmol, 98% Sigma-Aldrich) were dissolved in 500 mL degassed Milli-Q water in a round bottom flask. One drop of concentrated HCl solution (37% Sigma-Aldrich) was added to prevent premature precipitation. The flask was then purged with argon to remove air. The solution was magnetically stirred at 40°C. Ammonium hydroxide NH<sub>4</sub>OH (20 mL, 28% Sigma-Aldrich) was injected rapidly. The solution was stirred for 30 min, followed by the addition of oleic acid (6 mL, 90% Sigma-Aldrich). The reaction mixture was then heated at 80°C for 30 min before cooling to room temperature. The resulting fluid suspension was transferred to an Erlenmeyer flask. The black product that had adhered to the surface of the stir bar was discarded. Nanoparticles were

precipitated with 50 mL of ethanol (95%, ACP Chemicals) and collected with the help of a magnet. The clear supernatant was decanted. For each washing cycle, 10 mL of hexane was added to disperse the nanoparticles. After sonication for 10 min, the undispersed large aggregates were removed by transferring the black liquid phase containing dispersed magnetite nanoparticles to another Erlenmeyer flask. Subsequently, 20 mL of ethanol (95%) was added to precipitate the nanoparticles. After 5 min, the clear supernatant was decanted with the help of a magnet. The standard washing cycle with hexane/ethanol (1:2 as before) was performed three times. After the three washing cycles, the nanoparticles were washed with 20 mL ethanol. The washed Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dried overnight under vacuum prior to use.

#### 2.5.2 Preparation of ferrofluids and their patterning

For the "Standard" sample, a 25 wt% MNP ferrofluid was prepared as follows. Dried Fe<sub>3</sub>O<sub>4</sub> nanoparticles (~40 mg) were transferred to a vial, to which was added octane (~120 mg, 98%, Sigma-Aldrich). The suspension was mixed thoroughly in a sonication bath until homogenous.

The as-prepared ferrofluid was deposited into a polystyrene petri dish (Corning, Falcon Dish 35x10mm Easy Grip). The sample was then placed above a NdFeB N52 permanent magnet (DX06-N52, K&J Magnetics) at a well-defined distance controlled by a linear translation stage. The sample was then allowed to evaporate. Images and videos were captured and recorded by an optical microscope equipped with a CMOS camera (Thorlabs).

Magnetic field dependence: The distances between the magnet and the standard ferrofluid samples are adjusted to 5 mm, 7.5 mm, 10 mm, 12.5 mm and 15 mm for the magnetic field of 250 mT,

190 mT, 140 mT, 100 mT and 80 mT, respectively. All other conditions were kept the same. Five patterns were obtained for each of the different magnetic fields.

Concentration dependence: A magnetic field of 140 mT was used here. The quantity of MNPs is fixed at 33 mg for each sample. A stock solution of 33 wt% MNP ferrofluid was prepared. For lower concentrations, extra octane solvent was added to dilute the stock ferrofluid to the desired concentration. The total mass for ferrofluids with concentrations of 33 wt%, 25 wt%, 20 wt%, 15 wt%, 10 wt%, 5.0 wt% and 1.0 wt% are 100 mg, 132 mg, 165 mg, 220 mg, 330 mg, 660 mg and 3300 mg, respectively.

Evaporation rate dependence: Three standard ferrofluids were used with an applied magnetic field of 140 mT. One sample dish was covered by a glass slide half-way to give the "Moderate" sample and another one covered fully with a cap to give the "Slow" sample. For the "Fast" sample, a hot air flow was generated by a heat-dissipating fan in a microscope light source and directed to the ferrofluid surface to accelerate the evaporation rate.

Solvent dependence: A magnetic field of 140 mT was used. Solvent hosts of *n*-Hexane (99%, Sigma-Aldrich), *n*-heptane (99%, Sigma-Aldrich), *n*-nonane (99%, Sigma-Aldrich) and *n*-decane (99%, Sigma-Aldrich) were used here to suspend the dried MNPs.

Substrate dependence: Borosilicate glass substrates (Supa Mega Slides  $75.2 \times 50.4$  mm) were purchased from Electron Microscopy Sciences. A Teflon evaporating dish was purchased from VWR Canada. Silicon wafers 150 mm <100> were obtained from Nova Electronic Materials. All substrates were cleaned by sonication in an acetone bath, then in a deionized water bath and finally in a piranha solution (3:1 mixture of 98% sulfuric acid and 30% hydrogen peroxide) for 30 min each. Subsequently, the substrates were rinsed with deionized water and allowed to dry prior to use.

## 2.5.3 Magnets and magnetic field strengths

Neodymium Iron Boron permanent magnets (DX06-N52, K&J Magnetics) have cylinder geometry with radius of 25.6 mm and height of 9.5 mm. The magnetic field strength was measured with a gaussmeter (GM2, AlphaLab Inc.) and the magnetic flux density was estimated with COMSOL Multiphysics (**Figure 2.9**).



**Figure 2.9** Magnetic Field simulation of the disk permanent magnet with COMSOL Multiphysics. (A) Top view and (B) side view of the magnetic flux density of the disk magnet used in these experiments. The white bar in (B) locates the position of the sample at 10 mm for a 140 mT field. (C) Variation in the magnetic flux density from the center to the disk magnet edge. (D) Crosssection of the magnetic field where the samples are placed in the yz plane. The simulated magnetic field strength in (C) is matched with the experimental value measured with a gaussmeter.

# 2.6 Supporting information

## 2.6.1 Image processing details

We analyzed the Rosensweig patterns using the MATLAB (R2019a) image processing toolbox. Briefly, the image of interest was split into three RGB channels, where the spike positions were then filtered out by thresholding. The threshold RGB channels were combined to yield a blackand-white (bit-mapped) image. The small noise is filtered out by the *strel* function. From there the centers and diameters of the circles were extracted by the *regionprops* function. Red circles were then drawn on the original image to confirm that the right information was retrieved (see Figure below).



**Figure S2.1** Left panel shows the final recognition of the spikes indicated by red circles. Right panel shows the black-and-white binary (bit-mapped) image from the original RGB image of the Rosensweig pattern of interest.

The numbers of spikes in the patterns were then counted and the centers of the spikes were assigned coordinates. The coordinates were used to calculate the distances between the spike maxima to determine the wavelength. Defect densities of the patterns were identified through the standard

deviation of the calculated wavelengths: the larger the standard deviation, the higher the defect density. Voronoi diagrams were generated using the *voronoi* function with the coordinates and the Voronoi entropy was then determined to estimate the order of the patterns.

#### 2.6.2 Scalability of the pattern

The size of the trapped patterns described in this Chapter is limited by the quantity of MNPs and the size of the magnet. The trapped patterns can be scaled up when the MNP quantity and/or the magnet size increase. Here we explore the effect of increasing ferrofluid mass on pattern formation. With the same ferrofluids of 25 wt% MNPs in octane, we made the patterns with different starting fluid mass in the same magnetic field of 140 mT (**Figure S2.2**). The Voronoi entropy of the trapped patterns was found to remain consistent at ~1.1. Other parameters, including *h*, *d*, *N*,  $\lambda$  and  $\sigma$ , were observed to increase with the increase in starting fluid mass (**Table S2.1**).

**Table S2.1** Parameters of the trapped patterns obtained from the same ferrofluids of 25 wt% MNP with different fluid mass at the beginning. Units: mm (except for  $\sigma$  and *Svor*).

Fluid mass	56 mg	132 mg	165 mg	220 mg	330 mg
h	1.45	1.51	1.73	1.82	2.06
d	0.606	0.738	0.753	0.795	0.952
Ν	40	75	78	87	104
λ	1.28	1.22	1.33	1.34	1.46
σ	0.166	0.10	0.113	0.140	0.285
Svor	1.16	1.07	1.15	1.10	1.08



**Figure S2.2** The trapped patterns from different starting fluid mass with the identical ferrofluid of 25 wt% MNPs in octane in a 140 mT magnetic field. (A) 56 mg ferrofluids (B) 165 mg ferrofluids (C) 220 mg ferrofluids (D) 330 mg ferrofluids.

## 2.6.3 Additional figures



**Figure S2.3** Hysteresis loop of polydisperse MNPs at room temperature. The saturation magnetization of the MNPs is 73.3 emu/g by SQUID magnetometry.



**Figure S2.4** Images captured from the videos showing **Stage II** of spike evolution in the evaporation rate control study. The wavelength increases from "Fast" to "Slow".



**Figure S2.5** Images captured from the videos showing **Stage IV** of spike emergence in the solvent study.



Figure S2.6 Images captured from the videos showing Stage I in the substrate study.

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# Chapter 3 Macroscopic Pattern Formation in Evaporative Ferrofluids: The Role of Excess Oleic Acid

## 3.1 Abstract

Two well-known ferrofluid morphologies, the hexagonal spike and the labyrinthine patterns, were previously obtained separately from different interfaces. The two kinds of patterns are in essence driven by self-organization of magnetite nanoparticles in an applied magnetic field. Here we describe the impact of excess oleic acid (OA) on pattern formation in ferrofluids that results in a series of patterns—the hexagonal patterns transition to the labyrinthine patterns. The pattern transition is induced by an increase in the quantity of excess OA in the fluid medium. A defective pattern is obtained when OA is in excess. The ordered hexagonal array state resumes when the quantity of OA reaches a critical value ~5.2 wt% for 14.8 nm spherical MNPs. The rigid packing of OA chains in the stable MNP superstructures is confirmed with Fourier transform infrared spectroscopy (FTIR). During evaporation, we suggest that excess OA participates in pattern formation at three levels: 1) induce depletion attraction to guide MNP assembly, 2) change the fluid flow dynamics and 3) serve as a host for emergence of the labyrinthine pattern.

## 3.2 Introduction

Patterns are ubiquitous in natural and artificial systems. Patterns can exhibit bewildering complexity over many length scales. In biological systems, patterned structures that span the nanoto the micro-scale are often linked to functions. Diffraction of light from structured chitin nanophotonic features in butterfly wing scales results in brilliant iridescent colors, which provide for camouflage, thermoregulation, and signaling.<sup>1</sup> The lotus leaf is well-known for its non-wetting superhydrophobic surface that features unique hierarchical micro/nanoscale structures.<sup>2</sup> The morphogenetic origin of patterns of zebra stripes, when cast in the Turing reaction-diffusion framework to deposit melanin over space and time, may offer the animal protection by warding off disease-bearing insects.<sup>3</sup> Dynamical macro-patterns formed by schools of fish have prompted models of self-organization that are characteristically nonequilibrium.<sup>4</sup> In artificial systems, patterns may arise from the spatial or spatiotemporal distribution of building blocks during selforganization. The self-organized structures result from the space- and time-variation in the multilevel interactions of the building blocks coupled with all elements within the system, e.g. their host, or other "uninvited" impurities. Details of the resulting structures depend sensitively on the processes and pathways during self-organization. Features of self-organizing evaporative ferrofluids were described in Chapter 2, where changes in material and magnetic field parameters were shown to modulate the self-organization process of Rosensweig-like patterning.

Among the artificial systems that generate patterns, ferrofluids are exceptionally interesting because they can form a variety of steady-state patterns in response to different magnetic fields. Ferrofluids are colloidal suspensions of magnetic nanoparticles (MNPs) that are often stabilized with fatty acid ligands like oleic acid (OA). When excited by a sufficient magnetic field normal to

a nominally flat ferrofluid free surface, the film deforms under the magnetic force to a pattern of spikes. This is the Rosensweig normal field instability. The resulting patterns exhibit hexagonal or square lattice symmetry. Ferrofluids can also evolve into patterns of labyrinths, stripes, foams, bubbles, or rings when the fluid is confined in a Hele-Shaw cell.<sup>5-7</sup> The richness of patterns in ferrofluid systems originates from the delicate balance of nanoscale forces among self-organizing MNPs in an applied magnetic field.<sup>8,9</sup> A classic non-volatile ferrofluid can be considered as a static system, where, for example, the macroscale Rosensweig and the labyrinthine patterns exist in steady states sustained by an externally applied magnetic field. Once formed, these patterns no longer evolve over time. They remain stable without the need for injection of additional energy. Their morphology, patterning, and characteristic length scale correspond to a minimum in the system energy for a given set of conditions.

In this Chapter, we describe our research into ferrofluid systems comprising *fugitive solvent hosts* and the impact that excess oleic acid surfactant ligand has on the generation of the Rosensweig spike pattern, the labyrinthine pattern and combinations of both patterns. In contrast to instantaneous pattern formation in classic ferrofluids, evaporation driven fluid dynamics is now combined with the ferrohydrodynamic response in determining the temporal and spatial evolution of patterns. We assign a special role to excess oleic acid (OA) ligand in the evaporative ferrofluids. Ordered, stable hexagonal patterns of spikes emerge from evaporative ferrofluids formulated with no excess OA. Increasing quantities of excess OA leads to highly defected hexagonal patterns. A threshold OA excess is identified where a new ordered hexagonal state emerges. Beyond this threshold, coexisting labyrinthine-hexagonal phases evolve. This state eventually transitions to the fully labyrinthine phase.

The labyrinthine phase is particularly interesting because, unlike solid films, long-range (dipolar) interactions are necessary to form the undulating structures in fluid media. Wrinkled textures result when coupled materials grow at different rates. The more rapidly growing material must wrinkle in order to remain coupled with the other material. In coupled Hookean solids, the wrinkles that form are sustained by elastic stresses in the materials. A ferrofluid with a free surface cannot normally support shear stress, which is why dipolar interactions are important. In this Chapter, we introduce an intriguing twist on labyrinthine pattern formation by coupling evaporation induced solidification with fluid flow. It appears that the OA ligand plays a determining role in this process.

Infrared spectroscopy of the OA ligand provides insight into its role in the emergence of the hexagonal and labyrinthine phases. The ratio of the intensity of the asymmetric  $(v_{as})$  and symmetric  $(v_s)$  CH<sub>2</sub> stretching modes is correlated to the macroscopic order in the series of patterns. In the context of evaporation-mediated pattern formation, the oleic acid ligand serves as a morphogen that alters interactions between MNPs under a magnetic field and perturbs fluid surface tension under dynamic flows during host evaporation. The morphogen induces a non-uniform/gradient distribution over time that leads to the unique patterns.

# 3.3 Results and Discussion

Spherical magnetite MNPs were prepared by thermal decomposition of iron oleate in octadecene at 320 °C.<sup>10</sup> The MNPs have an average diameter of  $14.8 \pm 0.097$  nm by transmission electron microscopy (TEM). The MNPs are superparamagnetic at room temperature with a saturation magnetization of 73.6 emu/g (**Figure S3.1**). Excess OA was removed from the samples by repeated washing cycles with methanol until no large chunks of solids were observed in the wet powder of

MNPs. This initial washing to remove excess ligands is important to obtain reproducible results as described in the following section (see Methods for details). After washing, thermogravimetric analysis (TGA) revealed 14.7 wt% of organic content in MNP powders (see supporting information Section 3.6.3). The resulting free-flowing MNP powders are redispersible in alkane solvents.

#### 3.3.1 Pattern formation in nonane ferrofluids with excess OA

The experimental setup is identical to that described in Chapter 2. Accordingly, magnetite nanospheres were dispersed in *n*-nonane at 25 wt%. The suspension appears as a black homogenous mobile fluid suspension with no visible precipitate. This fluid was dispensed in the absence of a magnetic field onto a borosilicate glass substrate, wetting the surface completely. When the magnetic field is applied, the ferrofluid responds by a fluid flow that results in contraction of the mass of fluid away from its original outer physical boundary, the appearance of a contact angle, and formation of a large convex fluid "droplet". In the early stage of solvent loss, the fluid magnetization is below the threshold (critical magnetization)  $M_c$  to deform the fluid to begin pattern formation. The critical magnetization in this case is given by

$$M_{c}^{2} = \frac{2}{\mu_{0}} \left( 1 + \frac{\mu_{0}}{\mu} \right) \sqrt{\frac{d}{dz} (\mu_{0} H M) \gamma}$$
(3.1)

where  $\mu_0$  is permeability of vacuum,  $\mu$  is the permeability of the ferrofluid, H is the applied magnetic field,  $\gamma$  is the interfacial tension, and M is magnetization.

The pattern labeled **S0** in **Figure 3.1** shows an aerial view of the black fluid surface below the threshold. The white ring is due to the reflection of the annular light source that is used to

illuminate the surface in order to record video and capture still images as patterns emerge. The pattern **S0** is the identical starting point for all patterns that we describe in this study. The nonane solvent evaporates slowly at room temperature while the ferrofluid is exposed to a non-uniform magnetic field created by a permanent disk magnet. As the solvent evaporates, the magnetization M of the ferrofluid increases towards  $M_c$ . Since M = m/V, and the magnetic moment m of MNPs remains unchanged in a static magnetic field, only the volume of the fluid V decreases as the solvent evaporates. When the magnetization reaches  $M_c$ , the ferrofluid film undergoes a symmetry-breaking transition to yield a hexagonal pattern. The hexagonal pattern becomes permanently trapped when the nonane has fully evaporated. We refer to this as a kinetically trapped state; unlike a conventional ferrofluid, the trapped state does not relax and disappear when the magnetic field is removed. With no excess ligand, this trapped state is evident in the pattern **S1** in **Figure 3.1**.



**Figure 3.1** Patterns formed from the evaporative ferrofluids doped with increasing quantity of oleic acid (OA): **S0**, the initial homogeneous state (identical for all patterns); **S1**, the trapped state pattern with no excess OA; **S2** the pattern with 3.0 wt% excess OA; **S3**, the pattern with 5.2 wt% excess OA; **S4**, the pattern with 10.8 wt% OA; **S5**, the labyrinthine pattern with 22.4 wt% OA. Except for **S0** and **S5**, the corresponding Voronoi diagrams are given immediately to the right of each pattern. Hexagons colored in green are guide to the eye for order.

Regions of hexagonal symmetry can be located in pattern S1. These are most easily discerned by examining the Voronoi mapping to the right of the color image. A 3.0 wt% excess of OA was then added to the starting formulation while maintaining the MNP loading fixed at 25 wt%. The resulting pattern is shown in Figure 3.1-S2. For both S1 and S2, disorder due to the defects is evident from the entropy extracted from the Voronoi analysis (This analysis is discussed later in Section 3.3.2). There are clearly more defects in pattern S2. Visible light microscopic investigation of pattern S2 reveals that in addition to the defects, the spikes are irregular in size and shape. In pattern S2 we can identify other features. The outer perimeter of the dark disk of material is decorated with periodic corrugations that resemble a physical ring Bragg grating. The grating ridges point along rays that converge radially inward towards the center of the pattern. The flow field for the pattern is evident beyond the disk perimeter in the translucent pale orange thin film that covers the glass substrate. In fact, this pattern is shown for the samples S0 through S3. Images S0 to S3 also appear to evidence the so-called "coffee ring effect". This is the thin dark ring that is visible in the same orange film outside the circular perimeter of either the unpatterned fluid (S0)or the Rosensweig patterns S1 and S2. The ring may result from drying within the thinning film of fluid colloid suspension and pinning of the three-phase contact line during the convective flux driven by nonane evaporation.

When the quantity of OA is increased to 5.2 wt%, we obtain the pattern **S3** shown in **Figure 3.1**. The pattern has evolved into a well-ordered hexagonal lattice. This is the *critical value* of excess OA for our spherical MNPs to yield well-ordered hexagonal phases, below which the patterns will be defected. The Voronoi entropy has dropped to 0.843. We find that the transition from the defected hexagonal lattices **S1** and **S2** to the more ordered state **S3** is abrupt. Patterns exhibit more disorder when the amount of added OA is less than 5.2 wt%. For OA additions greater than 5.2 wt%, we observe a transition first to a joint but not intermixed phase of labyrinthine and hexagonal patterning (S4). In Figure 3.1, the labyrinthine phase in S4 is distinctly visible at the ring perimeter where it resembles a wrinkle pattern. The labyrinth texture appears only when the OA content reaches 22.4 wt% (S5). Beyond this OA doping level, the MNPs start to agglomerate in the fluid host.

#### 3.3.2 Pattern parameters

To quantify the order of patterns, Voronoi diagrams were constructed (**Figure 3.1**, for more detail see Chapter 2, Section 2.6.1). The probabilities  $P_n$  of the Voronoi polygons with n sides were determined. The Voronoi entropy  $S_{vor} = -\sum P_n \ln P_n$  was then calculated.<sup>11</sup> The more ordered the pattern, the lower the Voronoi entropy. Pattern **S2** has the largest Voronoi entropy and highest inter-spike wavelength. Pattern **S3** with 5.2 wt% excess OA has the lowest number of defects and the lowest Voronoi entropy. To the eye, the order of pattern **S1** appears comparable to that of **S3** but the Voronoi entropy in **S1** is increased by the appearance of defects among spikes at the pattern edge. To offer more insight into how the patterns evolve, **Figure 3.2** plots the spike number *N* and the peak-to-peak wavelength  $\lambda$ . The number of spikes in the patterns increases from **S1** to **S2**, and then decreases from **S2** to **S5**. The wavelength  $\lambda$  of the hexagonal array in the patterns does not follow any trend with the quantity of excess OA.



Figure 3.2 Plot of the number of spikes N (black) and the wavelength  $\lambda$  (blue) of the hexagonal patterns versus the amount of excess OA (mass fraction). The error bar is the standard deviation of the wavelength.

## 3.3.3 Spike surface anatomy: superlattices of MNPs

Though proof has been lacking, there is broad consensus that Rosensweig spikes most likely consist of uniaxially ordered chains of MNPs. Because conventional ferrofluids are dissipative systems, the characteristic spike patterns they produce when coupled to the magnetic field collapse when the field is reduced to zero. As we have argued in Chapter 2, the dissipative behavior of ferrofluids makes it difficult to examine the ensemble of the spike patterns and the spikes, together with their underlying mesostructure. Thus in this respect, little is actually known about how the MNPs are organized within the spike structures, and what this organization might reveal about spike morphogenesis, and ultimately how spike morphogenesis might be linked to the macroscale patterns. By trapping the MNPs in a spike cone, we can examine the surface anatomy of a spike by high resolution scanning electron microscopy (SEM).



**Figure 3.3** High resolution SEM of a spike obtained from the center pattern **S1**. (A) an area near the cone tip. The image was acquired from the region indicated in the red highlight of the cone icon at the top left. (B) a surface region near the base. The inset in the right panel shows a grain surface plane where the spherical MNPs are packed in a rhombic lattice.

**Figure 3.3** shows the arrangement of MNPs at the top and bottom regions of the surface of a spike. The spike was obtained from the center of pattern **S1** (no added oleic acid). In the tip region, we observe short-range ordered chains of spherical nanoparticles. Some chains are packed side-by-side in a square lattice (solid rectangle), whereas others pack in different orientations with interchain sphere neighbors staggered with respect to each other (dotted rectangle), and still others show short-range hexagonal/rhombohedral packing (circle). Simulation of the magnetic field for a ~10 mm magnetized cone shows that the field lines run almost parallel from the base (south) to the tip (north) where they are strongly concentrated.<sup>12</sup> While nanoparticle chains clearly form at the tip surface, it is surprising that the tip surface shows none of the long-range alignment suggested by the orientation of the field lines. Perhaps we are looking at a record of the effect of turbulence and particle pinning combined with MNP precipitation at the air/ferrofluid interface due to more rapid evaporation of solvent from the spike tip. Rapid quenching of nanoparticle and

aggregate motion during evaporation might lead to the type of short chain orientations we observe near the spike tip. We caution that our SEM experiment probes only the surface and near subsurface region of the spike, and so we do not know what the internal arrangement of MNPs in the tip looks like.

Scanning electron microscopy images acquired from areas sampled in the bottom region of the spike show clear longer-range rhombic lattice packing. In **Figure 3.3B**, a sample of the surface region comprises a patchwork of uncorrelated plane orientations with grain boundaries defined largely by defects and vacancies. The inset shown in the figure confirms that the MNP spheres are arranged on a rhombic lattice. This makes sense, since theoretical and experimental studies of chains of magnetic nanoparticles reveal that minimum energy configurations are those for which the head-to-tail dipolar interactions are favored when spheres on adjacent chains are staggered with respect to their lateral neighbors.<sup>13</sup>



**Figure 3.4** (A) SEM image of the surface and near sub-surface of nanoparticle lattices near the base of a conical spike. The arrows point to holes where the next lattice layer is visible. (B) A crack on the spike surface showing the underlying nanoparticle ordering.

**Figure 3.4A** zooms into the surface region at the spike base. The surface shows a well-ordered rhombic lattice that is populated by vacancy defects and inclusions of somewhat larger magnetite nanoparticles. The arrows locate gaps in the surface lattice plane. The gaps are bordered by some larger MNPs. Beneath the openings, the underlying order of the next lattice plane is visible. The underlying MNPs are visible in a crack on the surface shown in **Figure 3.4B**. The spikes have curved surfaces so that the planar texture we observe must curve in space. It makes sense, given these images, that the spikes can be viewed as having a type of onion ring layering. In Chapter 4 we will show that thermally treated spikes exhibit clean longitudinal, radial and circular fracture lines, as well as interlayer peeling that sheds curved fragments. From the above SEM images, it is probable that the fracture lines propagate along various easy directions among aligned nanoparticles. Peeling of thin sections is governed by the ease of separating curved planes of nanoparticles.

## 3.3.4 Nanoscale interactions among MNPs

It is clear that OA governs some aspect of adhesion among nanoparticles that make up the trapped spikes that form the pattern. In our experiments with the fugitive fluid host, we end up changing the volume through evaporation at a fixed external magnetic field. Volume and solvent properties are also control parameters. As we explained in Chapter 2, volume contraction due to solvent loss causes the magnetization of the sample to increase to  $M_c$  required to initiate pattern formation. A spike pattern emerges, but as the solvent continues to evaporate, MNPs are no longer solvated. When a solubility threshold is reached, nanoparticles must begin aggregating (precipitating) under influence of the magnetic field. Something else must then assist in sustaining the spike pattern is that

the oleic acid ligands must be interacting through noncovalent bonds. Oleic acid is therefore also a control parameter, which is why we became interested in exploring the effect of excess ligand on patterning. In this context, it is helpful to take a closer look at the competition between nanoscale forces when MNPs are brought very close together, as we conjecture happens when we make the trapped spikes.

First, we should remind ourselves what ingredients are necessary to sustain regular patterns and see how OA might affect them. In short, we require that the building block nanoparticles must interact at the system level through (1) short-range repulsive interactions; (2) medium-range attractive interactions; and (3) long-range repulsive interactions.<sup>9</sup> In our ferrofluid system, the short-range interactions arise largely from steric repulsions among MNPs due to the OA ligand coating. Medium-range interactions are those that are embodied in the van der Waals (vdW) potential. The vdW attractions include the alkane fluid, the surface-bound OA ligands and MNPs. At the macroscopic level of the ferrofluid, the vdW interaction among the nonane molecules will manifest itself as interfacial tension, which tends to minimize the surface area of domain spikes that will form the pattern. The surface energy of the ferrofluid/air is given by  $E_S = \sigma S$ , where S is the area of the ferrofluid-air interface. Oleic acid, as a fluid host, has a surface tension of 32.79 mN m<sup>-1</sup>,<sup>14</sup> higher than 22.85 mN m<sup>-1</sup> that of nonane. The presence of excess OA in nonane will therefore increase the surface tension of the host fluid. When MNPs are in contact ( $\delta \ll a$ ), the magnitude of vdW interactions between two spherical MNPs with radius a coated with a single layer of oleic acid of thickness,  $\delta$ , is given by  $U_{vdW} \approx -\frac{Aa}{12\delta} = -\frac{22 \times 10^{-21} \times 7.4 \times 10^{-9}}{12 \times 2.2 \times 10^{-9}} =$  $6.2 \times 10^{-21}$  J, or ~1.5 k<sub>B</sub>T. Here A is Hamaker constant of magnetite nanoparticles taken from reference (15). The long-range repulsive interactions are due to magnetic dipoles of the MNPs. As

described in Chapter 1, the dipole-dipole interaction can be attractive or repulsive. In our configuration of ferrofluids exposed to a perpendicular magnetic field, the number of MNPs placed side by side (repulsive interaction) far exceeds the number of head-to-tail attractive. On average then, the repulsive dipolar interactions dominate. (This case will be reversed if the magnetic field is applied parallelly.) For two magnetite nanoparticles with  $M_s = 73.6 \times 5.17$  emu cm<sup>-3</sup> = 380.5 kA m<sup>-1</sup> and  $a = 7.4 \times 10^{-9}$  m, the magnitude of the dipolar attraction at contact ( $r \approx 2a$ ) is given by  $U_{dd} = \frac{m^2}{2\pi\mu_0 r^3} = 2.56 \times 10^{-20}$  J or ~6.3  $k_BT$ . For MNPs aligned antiparallel, the magnitude of the dipolar repulsion  $U_{dd} = \frac{m^2}{4\pi\mu_0 r^3} = 1.28 \times 10^{-20}$  J or ~3.2  $k_BT$ . This simple heuristic estimation suggests that the dipolar repulsion is roughly two times stronger than the vdW attraction between MNPs. When solvents evaporate fully and the applied field is removed, vdW attractions between the OA ligand must compensate for this energy difference to stabilize the spike superstructure. The distance between OA alkyl chains must then be small to have a strong vdW attraction. We probe this next by studying OA-OA interactions by vibrational spectroscopy.

## 3.3.5 FT-IR Spectroscopy Analysis

Vibrational spectroscopy can offer insight into surface-bound oleic acid and possible local ligandligand interactions. We used Fourier Transform Infrared spectroscopy (FT-IR) to probe vibrational modes of spike and labyrinthine features (MNP-OA composites) extracted from sample **S1–S5** patterns of Section 3.3.1. The resulting IR spectra are collected in **Figure 3.5**. Our notation can be understood as follows: "s" stands for spike and "I" stands for labyrinth. The lower-case letters are appended to the sample reference **S1–S5** to show what spectrum is assigned to a spike and what to a labyrinth. Intense absorptions located in the low wavenumber range, 550–588 cm<sup>-1</sup>, are observed for all MNP-OA composites, **S1s–S5l**. These are assigned to Fe–O modes in the crystalline lattice of magnetite (Fe<sub>3</sub>O<sub>4</sub>).<sup>16, 17</sup> The remaining vibrational features belong to the OA ligand. A complete assignment of the bands is given in **Table S3.3**.



Figure 3.5 FT-IR spectra of spike (s) or labyrinth (l) features obtained from the patterns S1–S5. Reference spectra are given at the top for the MNPs functionalized with a single layer of OA, and at the bottom for neat OA. (A) Stacked spectral scans of spike/labyrinth features from samples S1–S5. (B) Magnification of the  $\nu$ (CH<sub>2</sub>) stretching region 2800–3000 cm<sup>-1</sup>; (C) the  $\rho$ (CH<sub>2</sub>) rocking region between 600–800 cm<sup>-1</sup>. See text for explanations.

 $v(CH_2)$  stretching. The modes assigned to C–H stretching are located between 2800–3000 cm<sup>-1</sup>. In neat liquid OA (bottom spectrum in **Figure 3.5A**), two prominent bands arise in the CH<sub>2</sub> stretching region. These correspond to the  $v_s(CH_2)$  symmetric stretching mode at 2854 cm<sup>-1</sup> and the asymmetric  $v_{as}(CH_2)$  mode at 2923 cm<sup>-1</sup>. For spikes from samples **S1s** to **S3s**, the  $v_s(CH_2)$  modes of OA fall in the range 2844 to 2848 cm<sup>-1</sup>, while those for the more intense  $v_{as}(CH_2)$  mode

lie in the range 2900–2950 cm<sup>-1</sup>. It is well established that the characteristic CH<sub>2</sub> symmetric stretching mode of ordered orthorhombic or hexagonal packings of the fatty acid chains is located below 2850 cm<sup>-1</sup>, whereas a value above 2850 cm<sup>-1</sup> is typical for liquid phase fatty acids.<sup>18</sup> This mode is located at 2854 cm<sup>-1</sup> for liquid oleic acid. In IR spectroscopy, the wavenumber positions associated with the  $v_{s}(CH_2)$  and  $v_{as}(CH_2)$  stretching modes give qualitative information about the overall crystalline organization of alkyl chains in self assembled monolayers.<sup>19</sup> In vibrational spectra of self-assembled alkyl thiols on metal and metal oxide surfaces, it is customary to compare wavenumber shifts (and peak widths) associated with the  $v_{s}(CH_2)$  and  $v_{as}(CH_2)$  modes in the liquid phase and in the molecular crystal phase. A shift toward low frequency values is always observed when there is evidence of crystal-like packing. The shift to lower wavenumber is typical of a transition from conformational disorder in the fluid to conformations of the alkyl chains that are characteristic of the molecular crystal. It can be difficult to determine the wavenumber of the asymmetric CH<sub>2</sub> stretching mode precisely because of its proximity to the Fermi resonance and the in-plane CH<sub>3</sub> stretching frequency near 2960 cm<sup>-1</sup>. Therefore, we focus on the  $v_{s}$ (CH<sub>2</sub>) mode. This mode decreases from 2854 cm<sup>-1</sup> for neat OA in the liquid phase, to 2848 cm<sup>-1</sup> in the powdered sample of MNPs (top blue spectrum labeled "MNPs" in Figure 3.5), decreasing further to 2844 cm<sup>-1</sup> in sample S1s. For comparison the 0°C  $\alpha$ -phase of OA exhibits a band at 2850 cm<sup>-1</sup>, while its -10 °C  $\gamma$ -phase counterpart expresses the same vibration at 2848 cm<sup>-1</sup>.<sup>20</sup> We can then say that the OA on sample S1s is organized in a way that more closely resembles a solid-like structure than a fluid material. For sample S2s (3.0 wt% excess OA) we see that both the v<sub>s</sub>(CH<sub>2</sub>) and  $v_{as}$ (CH<sub>2</sub>) modes appear unshifted with respect to sample S1s. For sample S3s (5.2 wt% excess OA), the  $v_{s}(CH_2)$  mode is located at 2848 cm<sup>-1</sup>. It might be argued that OA in these samples is also structured among the MNPs. For the labyrinthine features in samples S4I and S5I, the  $v_{\rm s}$ (CH<sub>2</sub>)

modes locate between 2852–2854 cm<sup>-1</sup>. These values are comparable to neat liquid phase OA, meaning that the OA in labyrinthine features behaves similarly to neat OA.

	vas(CH <sub>2</sub> )	$v_s(CH_2)$	I <sub>as</sub> (CH <sub>2</sub> )	$I_{\rm s}({\rm CH_2})$	$R = I_{\rm as}/I_{\rm s}$
	$(cm^{-1})$	$(cm^{-1})$			
MNPs	2915	2848	0.1192	0.1271	0.938
S1s	2911	2844	0.1080	0.1158	0.933
<b>S2s</b>	2911	2844	0.5377	0.5659	0.950
<b>S3</b> s	2915	2848	0.5397	0.5492	0.983
S4s	2917	2852	0.5685	0.5203	1.09
<b>S4</b> I	2921	2852	0.4905	0.4155	1.18
S5I	2923	2854	0.4233	0.3293	1.29
Neat OA	2923	2854	0.4225	0.3288	1.28

**Table 3.1** FTIR frequency and absorption intensity of the asymmetric  $v_{as}(CH_2)$  and symmetric  $v_s(CH_2)$  carboxylate stretching mode, and the intensity ratios *R*.

In addition to the frequency shift, we observe that the relative intensity of the  $v_{s}(CH_2)$  and  $v_{as}(CH_2)$  bands also changes. The two bands are enlarged in **Figure 3.5B**. The intensity ratio *R* of the asymmetric and symmetric CH<sub>2</sub> stretching modes from Raman spectroscopy has been used as an indicator of the chain packing density, according to:<sup>21</sup>

$$R = \frac{I_{\rm as}}{I_{\rm s}} \tag{3.2}$$

where  $I_{as}$  and  $I_s$  are the intensity of the asymmetric and symmetric CH<sub>2</sub> stretching modes. Adapting this method to IR spectroscopy, *R* values based on sample **S1s–S5I** might be used to predict ligand
organization within the pattern features. Accordingly, we calculated the R values which are given in **Table 3.1**. We can see that labyrinthine features **S4I** and **S5I** have R values that are close to those for the free OA. This is especially so for **S5I**. Interestingly, patterns that we observe with a high degree of symmetry according to the Voronoi entropy have R values close to unity (see **S3s** and **S4s**). As a simple metric, when excess OA is present in the system, an R value smaller than 1 means that patterning will yield a disordered (defected) hexagonal phase; and an R larger than 1 will yield labyrinthine features.

*Carboxylic acid vibration.* The C=O stretching mode in neat OA is located at 1708 cm<sup>-1</sup>. In the absence of excess OA ligand, as in powders of **MNPs** and **S1s**), the C=O peak is absent because OA ligands bind to the surfaces of MNPs via the chelating and bridging carboxylate head group. Instead, the asymmetric and symmetric COO<sup>-</sup> stretching modes appear in the region 1400–1600 cm<sup>-1</sup>. For sample **S2s–S5I**, the C=O stretching mode is present because there is free carboxylate acid in the matrix.

We turn our attention to the COO<sup>-</sup> stretch that overlaps with CH<sub>2</sub> bending in the region between  $1400-1460 \text{ cm}^{-1}$ . We assign the peak based on two reference points: IR spectra of the precursor MNPs and the neat OA. First, we identify three peaks in neat OA where the CH<sub>2</sub> bending is located at 1464 cm<sup>-1</sup>, the CH<sub>3</sub> bending at 1436 cm<sup>-1</sup> and the CH<sub>2</sub> adjacent to COOH at 1412 cm<sup>-1</sup>. Tracing the peak intensity and position, we assign the peaks observed in our samples to CH bending. These shift to lower wavenumber with decreasing OA. Therefore, the symmetric COO<sup>-</sup> stretching is not observable. The asymmetric COO<sup>-</sup> stretch is weak. The broad band in the region 2500–2700 cm<sup>-1</sup>

observed for sample **S2s–S5l** is assigned to the hydrogen bonded OH stretch, which is the tell-tale signature of a dimeric carboxylic acid.<sup>22</sup>

*CH<sub>2</sub> rocking band.* The CH<sub>2</sub> rocking vibrations are typically found at 722 cm<sup>-1</sup> for neat OA. It is well established that splitting of the CH<sub>2</sub> rocking band occurs in the solid/crystalline phase.<sup>23</sup> Splitting of the CH<sub>2</sub> rocking suggests a high degree of packing order like crystalline behaviour of the methylene group in these samples.<sup>22</sup> The rocking mode appears as a doublet in spectra acquired from samples **S1s**, **S2s** and **S3s**. Samples **S4s** and **S4I** may also show the doublet feature, but one of the peaks is obscured by the adjacent large band from Fe–O, as is evident in **Figure 3.5C**. The CH<sub>2</sub> rocking band recorded in sample **S5I** occurs at 722 cm<sup>-1</sup>, corresponding to the same position as that from neat OA, which shows only a single peak consistent with its fluid state.

Molecular organization of liquid OA is mainly associated with the interdigitated structure of OA dimers, which are formed by a head-to-head arrangement of the carboxylate groups.<sup>24</sup> This suggests how OA molecules might pack in the MNP superstructures doped with excess OA. With the information extracted from vibrational spectroscopy, we can suggest how excess OA participates in creating and stabilizing the superlattices of MNPs (**Figure 3.6**). In the absence of excess OA, a spike MNP superlattice is stabilized mainly by particle-particle single-layer ligand interdigitation in 3D. This is in line with the experiment of Jaeger et al. who proposed that ligand interdigitation is crucial to sustaining large-scale single layer nanoparticle-assembled 2D membranes with large Young's modulus.<sup>25</sup> Similarly, we argue that ligand interdigitation may imply significant surface density and packing geometry of the OA ligands on the magnetite nanoparticles that can be the "glue" that holds the spikes together. In addition to our electron

microscopy images, evidence of OA-OA and related stabilizing interactions would imply that our trapped Rosensweig patterns represent the 3D extension of the Jaeger construct.



**Figure 3.6** Proposed mechanism for trapping Rosensweig patterns according to additions of OA as a control parameter. Trapped spikes in the absence of free OA adopt of monolayer interdigitation to stabilize them. Trapped spikes that result in the presence of excess OA may have some degree of double layer interdigitation with interacting OA dimers. The non-rigid phase seen in the labyrinthine features is the result of partial dilution of solid phase free material that otherwise forces a transition into the labyrinthine architecture.

With excess OA, structures like spikes can be sustained as trapped objects by forming doublelayer interdigitation with dimers in between. The ferrofluid labyrinthine phase is particularly interesting since it is not observed except in the confines of a Hele-Shaw cell.<sup>26</sup> Clearly, the appearance of the labyrinth phase is related to the "fluidization" of the matrix by excess OA. We discuss this further in Section 3.3.7 below. From our FTIR analysis, we find that the macroscopic ordering is linked to the local packing of the ligand alkyl chain, specifically the balance of CH<sub>2</sub> symmetric and asymmetric stretching. In other words, the  $CH_2$  stretch intensity ratio R = 1 (indicating the local rigid packing of OA chains at the molecular scale) is associated with the macroscopic order in the trapped patterns.

#### 3.3.6 How does excess OA change the patterns?

The macro-patterns we have observed depend on the amount of oleic acid ligand added to the medium. Excess ligand is implicated in modulating features of the emergence and recording of macroscopic hexagonal patterns, and in particular, the appearance of the labyrinthine texture. This raises the question, what is the role of OA in regulating patterning?

In this regard, it is interesting that we find that a change in building blocks from spheres to cubes yields similar results when the formulations are nourished with excess OA. Addition of OA ligand in increasing amounts to magnetite nanocube based ferrofluids yields hexagonal, then defective hexagonal, then coexisting hexagonal-labyrinthine, and then labyrinthine patterns (see Section 3.6.2 for patterns of the cube series). These experiments tell us that block shape and even differences in magnetic anisotropy of the building blocks are not significantly strong control parameters with respect to oleic acid. To trace a pathway how OA perturbs pattern formation, we turn to the evolution process of these patterns from **S0** to **S1–5** (videos in the links "Non25\_S1", "Non25\_S2", "Non25\_S3", "Non25\_S4", "Non25\_S5"). From the videos, the pattern formation can be analyzed by two separate processes: the Rosensweig instability regime in the center of the fluid and the ring formation at the periphery. Correspondingly, we suggest that OA molecules perturb ordering of MNPs at the nanoscale in two aspects: they induce depletion attraction and promote the capillary flow. These are discussed separately below.



Figure 3.7 (A) Early snapshots of the lattices during pattern formation process of pattern S1, S2, S3 and S4. Red dots denote the peak of spikes in the pattern. (B) Proposed fluid dynamics within the evaporating ferrofluids: The left side reflects the system in the absence of OA where the inward Marangoni and ferrohydrodynamic flow dominate. The right side shows that the outward capillary flow is enhanced by excess OA, leading to the ring growth.

#### Examining the Rosensweig regime

We first observe that the pattern onset time increases with more OA added to the ferrofluids. Similar to the argument in Chapter 2, this increasing onset time suggests that  $M_c$  of ferrofluids increases with an increase in the quantity of excess OA. This can be understood by the fact that the presence of OA increases the surface tension of the host fluid. According to Equation 3.1,  $M_c$ increases with an increase in  $\gamma$ . The Rosensweig instability that governs pattern formation can be understood as magnetic field driven self-organization of MNPs at the nanoscale. In Section 3.3.4, we pointed out the key elements for self-organized ordering, which are the ligand steric repulsions, the vdW forces, the magnetic dipolar interactions. The ratio between the magnetic dipolar energy and vdW energy defines the magnetic Bond number  $N_{\rm B}$ :<sup>27</sup>

$$N_B = \frac{\mu_0 M H L}{2\gamma} \tag{3.3}$$

Here *L* is the characteristic size of the domains and  $\gamma$  is the interfacial energy. This *N*<sub>B</sub> provides a quantitative measure for the emergence of self-organized patterns according to the control parameters of the system.

To account for the high defect density in pattern S2, we examine the pattern evolution process in video "Non25\_S2". We observe that spikes first evolve in a coexisting hexagonal and square array (see Figure 3.7). The size of these two domains *L* is different, suggesting *N*<sub>B</sub> is different for these two phases. In sample S2, the presence of excess OA may change the interfacial energy  $\gamma$ . But this does not explain why two phases arise. Square symmetry has been observed in conventional non-volatile ferrofluids only when a high enough magnetic field *H* is applied (larger magnetization).<sup>28</sup> Magnetization *M* as a control parameter pushes the fluid into a new regime where internal variables like interparticle distances adjust to new length scales that result in energy minimization and reconfiguration of the spatial pattern consistent with the new energy minimum. But how does excess OA affect *M* as the applied *H* field is fixed?

We suggest that the emergence of square arrays in our fugitive solvent systems is due to local large aggregates of MNPs. The large aggregates result from depletion attraction. Depletion attraction comes into play when excess ligand is present in the ferrofluid. When two MNPs are brought close to each other, the free OA and nonane molecules are preferentially excluded from the vicinity in

between the two MNPs. The two MNPs are then "pushed" together by the fluid host. Depletion attraction can induce assembly of nanoparticles *in the colloidal suspension*,<sup>29-32</sup> therefore affecting the patterning at the early stage of evaporation. These large aggregate of MNPs will have greater *M* at the time of pattern onset, which produces square arrays on the left side (**Figure 3.7A-S2**). At this stage, the captured pattern is a metastable mixed square-hexagonal phase. With continuing evaporation, the system moves to a complex stage with three events happening simultaneously: new spikes emerge from the fluid front at the edge, some coalesce into the existing spikes, two spikes in the square-hexagonal lattice shrink their sizes. All of these events cause the lattice to rearrange, giving rise to penta-hepta defects. Eventually these defects are trapped in the pattern **S2** when nonane solvent evaporates completely (see video "Non25\_S2".). Solvent loss at the later stage does not offer one pattern regime or the other to domination until mutual adjustments create defects that become trapped—in this case the hexagonal phase more or less wins out.

During the formation of patterns **S1**, **S3** and **S4**, only the hexagonal array appears (see **Figure 3.7** and their corresponding videos). In sample **S1**, the hexagonal lattice remains unchanged throughout the evaporation. Spike fission at the periphery accounts for the slightly higher Voronoi entropy. Spike fission has been described in Chapter 2 due to changes in ferrofluid surface tension and field gradient.<sup>8, 33</sup> We observe no spike fission for samples **S3** and **S4**. Excess OA will increase the surface tension and therefore stabilizes the spikes against fission. A perfect hexagonal lattice is therefore retained for **S3** and **S4**.

The critical value of excess OA required to produce an ordered hexagonal pattern varies with MNPs. In another series of study with cubic MNPs (cube edge length l = 10.0 nm), this critical

value is found to occur at 7.0 wt%. In addition to the standard field of 140 mT. We apply two different magnetic fields to samples with an excess OA of 5.2 wt%. An ordered pattern is obtained with a stronger field of 250 mT (**Figure 3.8A**), with a smaller wavelength and a larger number of spikes (This is in line with the effect of magnetic field described in Chapter 2). Applying a weaker field of 80 mT results in a highly defected pattern despite that the excess OA is at the "critical" level (**Figure 3.8B**). Lowering the applied magnetic field strength results in a smaller magnetization of MNPs (see the M/H curve in **Figure S3.1**). The magnetic dipole-dipole interactions therefore weaken, unable to provide long-range order at the macroscopic level.



**Figure 3.8** Trapped patterns from nonane ferrofluids with 5.2 wt% excess OA under a magnetic field of (A) 250 mT and (B) 80 mT.

#### Excess OA promotes internal flows to ring formation

Now we examine the peripheral area. Comparing Video "Non25\_S2" to Video "Non25\_S1", a major feature arises at the beginning of evaporation: a black ring forms around the ferrofluid with a separation. We suggest that this ring formation is due to an OA stabilized balancing area where

an incoming thin layer of fluid from the outer area encounters the evaporating front of the bulk ferrofluid at the contact line. Subsequently, the bulk ferrofluid starts to feed the ring with fluid resembling a gear. The ring grows thicker with evaporation. The same ring formation and growth is also observed in the video "Non25 S3" and "Non25 S4". We believe that the ring growth is associated with the so-called coffee ring effect in which a ring deposit forms after a particle suspension droplet evaporates.<sup>34</sup> A previous study showed that surfactant concentration can alter the flow dynamics, i.e. outward capillary flow and inward Marangoni flow, within the evaporating fluid and therefore change the outcome of deposition.<sup>35</sup> In our systems, the flow dynamics inside the evaporating ferrofluid involve Marangoni flow, capillary flow and ferrohydrodynamic flow. These flows can transport matter (i.e. MNPs and OA) within the evaporating ferrofluid. During evaporation, solvent escapes from the contact line at a faster rate compared to the liquid/air interface,36 which results in a concentration gradient across the fluid. This gradient induces a capillary flow from the interior to the edge. The difference in evaporation rates also induces a surface tension gradient which causes Marangoni flow directing from the contact line to the top of the fluid near the surface. Both capillary flow and Marangoni flow exist in any evaporative fluid, with a strength difference depending on the fluid hosts, surfactants, particle concentration.<sup>37, 38</sup> Under a non-uniform magnetic field, MNPs experience a field gradient across the sample plane with a magnetic force pulling MNPs towards the lowest gradient area. The magnetic force is driven by the field gradient and given by  $F_m = V \mu_0 H \Delta \chi \nabla H$ . Here V is the volume of particles,  $\mu_0$  is the vacuum permeability, H is the applied magnetic field,  $\Delta \chi$  is the susceptibility difference between MNPs and nonane, and  $\nabla H$  is the field gradient. This gradient force accounts for the initial movement of ferrofluids towards the center of the substrate where the magnetic field is applied.

In the absence of excess OA ligands, the alkane-based ferrofluid system is dominated by Marangoni flow and ferrohydrodynamic flow. Most of the MNPs have been assembled into a pattern of spikes. No "coffee ring" is observed (pattern **S1**). The presence of free OA immediately promotes the coffee ring effect (pattern **S2**). Oleic acid is a surfactant, which lowers the surface tension gradient of the fluid and weakens the Marangoni flow. The capillary flow therefore dominates; this outward flow transports MNPs and OA molecules to the edge. The ring gets thicker with more OA (see videos). In turn, fewer MNPs will be available for spike formation. As a result, the number of spikes decreases with increased OA.

## 3.3.7 The emergence of labyrinthine features in pattern S4 and S5

In the opening to this chapter we wrote that unlike solid films, the labyrinthine phase requires longrange (dipolar) interactions to form the undulating features in fluid media. Wrinkles can emerge when materials that are coupled grow at different rates. Unlike coupled Hookean solids, a ferrofluid with a free surface is normally unable to support shear stress, making dipolar interactions important to their emergence. This argument holds well for conventional ferrofluids in the Hele-Shaw experiment, but why do we obtain the labyrinthine phase in our media? We believe the answer lies in the fact that our systems start out as fluids, but then in the course of volatile solvent loss, they take on solid-like character and become materials that can accommodate shear stresses like solids.

Starting in pattern **S3**, a radial band with fingering structures arises between the center spike pattern and the edge ring formation. The radial spoke-like structures become obvious in pattern **S4**, as evident in **Figure 3.9A**. In addition, the space between the spikes is filled with branch patterns. Under the optical microscope, we can see that these regions are covered by a transparent liquid oleic acid. The OA content is higher in this labyrinthine area than that in the spike (see TGA results of **S4s** and **S4l**). Since the starting ferrofluid is homogenous, the OA gradient in the trapped pattern develops over the course of pattern formation via strong capillary flow. **Figure 3.9B** shows that the MNPs in the OA matrix form chains in the direction of the applied magnetic field. The formation of the labyrinthine phase is probably due to the stress relief from the inter-chain repulsion within the composite.



**Figure 3.9** (A) A spike and its surrounding bridges are covered with a layer of OA in pattern **S4**. (B) The chain structures in the labyrinthine regions of pattern **S4**. (C)Tiny spikes floating in the "void" region of the labyrinthine pattern **S5**.

No ring formation occurs in pattern **S5**. From Video "Non25\_S5", the pattern formation process is pure splitting of the thick ferrofluid film. The voids of labyrinthine features evolve from elastic "cracking" of the MNP/OA composite during the last stage of solvent evaporation. The labyrinthine mountains are composed of chains, presumably from the linear aggregation of MNPs. Surprisingly, we observe tiny spikes in the "void" regions (see **Figure 3.9C**). These tiny spikes might be the lower scale assemblies of MNPs before they assemble into macroscale structures. The labyrinthine pattern **S5** relaxed after two weeks, i.e. the structure disappeared and appeared as

a dark paste. This suggests that the MNPs are not "locked" in these patterns where OA can act as a plasticizer and MNPs can move out of the "trapped" state in the composite. The original pattern cannot be obtained by reapplying the same magnetic field to the relaxed composite, i.e. no memory or hysteresis.

# 3.4 Conclusions

It should be noted that the as-synthesized MNPs are mixed with a large excess of octadecene and/or other unknown reaction by-products. The presence of these impurities is detrimental to the pattern ordering. **Figure S3.3** shows a number of examples where the MNPs were not washed clean enough and the corresponding patterns are highly defective. In turn, such pattern formation can be used to evaluate the "purity" of a batch of MNPs, either qualitatively by eyes or quantitatively using the Voronoi diagram as described in Chapter 2.

In summary, we demonstrated that excess oleic acid ligand regulates pattern formation in evaporative ferrofluids. By increasing the quantity of excess OA in the ferrofluid formulations, we obtain a series of trapped patterns from hexagonal spike pattern to labyrinthine patterns and the combination of the two phases. We report the nanoscale ordering of MNPs in the trapped spike superstructures. We investigate the role of OA in stabilizing the trapped MNP structures and suggest how OA affects the self-organization of MNPs from different aspects, which finally results in the change in the trapped patterns.

# 3.5 Experimental Methods

#### 3.5.1 Synthesis of magnetite nanoparticles

The magnetite nanoparticle synthesis was adapted from the procedures of Park et al.<sup>39</sup> All syntheses were carried out with a Schlenk line under argon. All reagents were commercially available and used as received.

*Iron-oleate complex*. 10.8 g of iron chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O, 40 mmol, Aldrich, 98%) and 36.5 g of sodium oleate (120 mmol, TCI America, 97%) were dissolved in a mixture solvent of 80 ml ethanol, 60 ml distilled water and 140 ml hexane. The resulting solution was heated to 70°C and kept at that temperature for four hours. After cooling, the organic layer containing the iron-oleate complex was washed three times with 30 ml distilled water in a separatory funnel. The organic layer was then dried over sodium sulfate and evaporated over a rotary evaporator. The resultant dark red liquid was dried under vacuum overnight.

Spherical Fe<sub>3</sub>O<sub>4</sub> nanoparticles. 7.20 g (8 mmol) of the iron-oleate complex and 1.14 g of oleic acid (4 mmol, Aldrich, 90%) were dissolved in 40.00 ml of 1-octadecene (Aldrich, 90%). The reaction mixture was degassed under a vacuum at 120°C for 1 hour, and then heated to 320 °C with a heating rate of  $3.3^{\circ}$ C/min and kept for an hour. The reaction flask was removed from the heating mantel and then opened in air after 20 min (the trick to oxidize MNPs). After about an hour, excess ethyl acetate (~ 100 mL) was added to the solution to precipitate the nanoparticles. After 15 min, the nanoparticles were separated with the help of a magnet. The black nanoparticles were washed with 60 mL of cyclohexane/ethyl acetate (1:5 v/v) for three times. Notice that the first supernatant is black, but the MNPs are retrieved by attracting them to the bottom of the flask by

the magnet. The nanoparticles were then washed with methanol multiple times to remove free oleic acid. For each washing cycle, 10 mL methanol was added to the wet nanoparticles. The unstable suspension was agitated by sonication for 3 min. The excess oleic acid is removed when the following conditions were met: 1) no chunks of solids were visible in the flask; 2) the wall of the flask was clear without adhesion of a film of oily matter; 3) the supernatant appeared transparent and colorless (the supernatant may be brown in the first few washes). Finally, the nanoparticles were dried overnight under vacuum to remove excess solvent.

## 3.5.2 Formulation of ferrofluids and patterning

A stock solution of oleic acid (Aldrich, 99%) in nonane was prepared. The concentration of oleic acid in the stock solution was increased by adding more oleic acid for each sample. For each sample, 30 mg of MNPs were dispersed in 90 mg of nonane/OA host. The mixture was sonicated for 15 min. Afterward, 100 mg of the homogenous ferrofluid was deposited onto a precleaned glass substrate. The sample was brought onto a NdFeB magnet (K&J Magnetics, DX06-N52) at a distance of 10 mm and allowed to evaporate. The pattern formation process was captured with an optical microscope.

#### 3.5.3 Characterization

FTIR spectra were recorded (4000–400 cm<sup>-1</sup>, 2 cm<sup>-1</sup> resolution) using a Bruker FTIR spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. For samples **S1s**, **S2s**, **S3s** and **S4s**, a few spikes were taken from their corresponding pattern. For samples **S4l** and **S5l**, the pasty labyrinthine features were scooped from their corresponding pattern. Neat **OA** was commercially available from Sigma–Aldrich, 99%. The sample **MNPs** was the washed product

from synthesis. Nanoparticles were imaged with FEI Tecnai G2 F20 transmission electron microscope (TEM) at 200 kV. The optical images and videos were acquired by a Thorlabs Compact USB 2.0 CMOS Camera mounted on an AMG optical microscope and a Keyence VHX-7000 Digital Microscope. The magnetic properties of MNPs were measured using a SQUID magnetometer (MPMS 3, Quantum Design). Magnetization curves of the magnetite nanoparticles were obtained over a range –7T to 7 T.

# 3.6 Supporting information

## 3.6.1 Characterization of MNPs



**Figure S3.1** (A) Transmission electron microscopy (TEM) image of spherical iron oxide nanoparticles. (B) TEM image of cubic iron oxide nanoparticles. (C) Hysteresis loops of the spherical and cubic iron oxide nanoparticles at room temperature.

## 3.6.2 Synthesis of cubic Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Cubic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized according to a previously reported method.<sup>40</sup> 7.20 g (8 mmol) of the iron-oleate complex and 2.44 g of sodium oleate (8 mmol, TCI America, 97%)

were dissolved in 36.0 g of 1-octadecene (Aldrich, 90%) and 4.00 g of diphenyl ether (Aldrich, >99%). The reaction mixture was degassed under a vacuum at 120°C for 1 hour, and then heated to 305 °C at a rate of 3.3°C/min and maintained at that temperature for 1 hour. The resulting solution was cooled to room temperature, and excess ethyl acetate was added to the solution to precipitate the nanoparticles. The nanoparticles were separated with the help of a magnet and washed with cyclohexane/ethyl acetate (1:5) cycles. Finally, the nanoparticles were dried overnight under vacuum to remove excess solvent.



**Figure S3.2** The trapped patterns from cubic MNP based ferrofluids with a different quantity of excess OA. The amount of excess OA is indicated in the upper right corner. Like the sphere series, the cube series shows the same ordered hexagonal to defective hexagonal to ordered hexagonal to mixed hexagonal-labyrinthine and to labyrinthine patterns.

#### 3.6.3 Thermogravimetric Analysis of the pattern S1–S5

We used thermogravimetric analysis (TGA) to quantify the OA content in the spikes and labyrinthine features in the **S1–S5** series. The results are summarized in **Table S3.2**. In general, we observe two distinctive weight losses for the MNP composites during the heating cycle. The two desorption processes of OA are attributed as physisorbed and chemisorbed OA on the MNP surfaces. For spike-form composites, the inflection points of the TGA curves occur at around 300 °C; for labyrinthine composites, they shift to lower temperatures. The total weight loss increases in the direction of OA increase, confirming that more OA is present in the composites.

Pattern	Step 1	Step 2	Weight Loss
S1s	5.0%	9.7%	14.7%
S2s	7.5%	12.8%	20.3%
S3s	8.7%	11.3%	20.0%
S4s	10.8%	13.7%	24.5%
<b>S4</b> l	15.0%	28.9%	43.9%
<b>S5</b> 1	27.4%	27.3%	54.7%

Table S3.1 Thermogravimetric analysis of the spike/labyrinth features from pattern S1 to S5.

For sample **S1**, the MNPs were washed multiple times to remove free ligand before the experiment. The weight loss of **S1** should correspond to the minimal amount of OA required to stabilize the corresponding MNPs in nonpolar solvents, however, the quantity of OA ligand on nanoparticle surface is often underestimated by TGA because of incomplete ligand decomposition. We can see that the amount of OA is overestimated (compared to what was added) when OA is in excess. Another complication is that OA can react with iron oxide nanoparticles under an inert atmosphere at elevated temperature. This reaction will lead to higher weight loss.

## 3.6.4 FTIR band assignment of samples from pattern S1 to S5

*Multiple bonding absorption region.* We observe several peaks in the region of 2400–1900 cm<sup>-1</sup>, for the powdered of MNPs and samples **S1s**, **S2s**, **S3s**, **S4s**, **S4l**. Infrared absorption in this region often relates to vibrations with a bond order of 2 or higher.<sup>41</sup> We assign the peak at around 2340 cm<sup>-1</sup> to stretching of gaseous  $CO_2$ .<sup>42</sup> The peaks found at around 2110 cm<sup>-1</sup> and 1995 cm<sup>-1</sup> are associated with metal (iron) carbonyl stretching.<sup>43</sup> We believe that the presence of these peaks is because  $CO_2$  from the atmosphere is captured by the magnetite nanoparticles in the composite. The peaks diminish in sample **S5l**, where the surfaces of the magnetite nanoparticles are covered with excess OA (**Figure 3.9**).

Assignment	MNPs	S1s	S2s	<b>S3s</b>	S4s	<b>S4</b> I	S51	OA
vas(CH2)	2915	2911	2911	2915	2917	2921	2923	2923
vs(CH2)	2848	2844	2844	2848	2852	2852	2854	2854
v(C=O)	N/A	N/A	1699	1707	1707	1707	1707	1708
vas(COO <sup>-</sup> )	n.v.	1524	1524	1534	1540	1552	1556	N/A
v <sub>s</sub> (COO <sup>-</sup> )	n.v.	n.v.	n.v.	n.v.	n.v.	n.v.	n.v.	N/A
β(CH <sub>2</sub> )	n.v.	n.v.	n.v.	n.v.	1457	1457	1459	1464
$\beta(CH_2)$ adjacent to	1401	1401	1401	1412	1412	1412	1412	1412
COOH <sup>22</sup>								
β(CH <sub>3</sub> )	n.v.	n.v.	1422	1428	1430	1432	1436	1436
v(C-O) <sup>44</sup>	n.v.	n.v.	n.v.	n.v.	1283,	1283,	1283,	1285,
					1248	1248	1246	1248
$\beta$ (C=C-H) <sup>44, 45</sup>	n.v.	n.v.	947,	944,	940,	938,	939,	936
			977	977	971	971	969	
ρ(CH <sub>2</sub> )	687,	<i>683</i> ,	683,	683,	n.v.,	n.v.,	722	722
	718	716	718	718	718	720		
v(Fe-O)	561	549	543	551	579	581	588	N/A

**Table S3.2** FTIR band assignment of the magnetite nanoparticles (MNPs), pattern features S1s toS5I, and neat OA.

Note: n.v. means a certain mode is not visible, probably embedded in a broad absorption.

# 3.6.5 Additional data



**Figure S3.3** A number of trapped defected patterns where the antecedent ferrofluids contain excess ligand or other reaction by-product impurities.

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# **Chapter 4 Permanent Encoding of Nano- to Macro-scale Hierarchies of Order from Evaporative Ferrofluids**

# 4.1 Abstract

Magnetic field-directed assemblies of magnetic nanoparticles (MNPs) in ferrofluids exhibit complex interconvertible metastable patterns and structures. Formally, ferrofluid patterns are unstable—they disappear when the magnetic field is removed. The present study shows that ferrofluid patterns can be "trapped" as kinetically stable structures that encode a surprising degree of morphological detail over nanometer to millimeter length scales. An external magnetic field is used to direct assembly of oleic acid-decorated magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles to make spike and labyrinthine patterns in volatile host solvents of heptane, octane and nonane. Solvent evaporation coupled with increases in sample magnetization drives pattern formation and its permanent recording. Use of a crosslinking siloxane polymer host yields remarkably different material responses. From the trapped states in both fluid systems, previously unreported hierarchies of order emerge in nanocomposite spike structures that also exhibit orientational and magnetic anisotropy. The possibility of designing hierarchical matter from initially uncorrelated MNPs is demonstrated by a directed solid-state transformation of the magnetic nanocomposite; the spikes template memory of their origin onto the transformation products.

## 4.2 Introduction

The origins of patterns in material systems continue to draw the attention of experiment and theory alike. An exciting feature of patterns is their bewildering complexity over many length scales. Among others, this complexity is evident in biological entities, their structures and ecosystems,<sup>1</sup> in aeolian landforms,<sup>2</sup> in dendrite formation,<sup>3</sup> in the wetting and drying of colloidal droplets,<sup>4</sup> in Bénard–Marangoni convection,<sup>5</sup> in ferrofluids,<sup>6</sup> and in the assembly of compositions of magnetic nanostructures.<sup>7</sup> While these systems may exhibit patterns at multiple length scales, there is a tendency in the research community to study the relationships among the multiple length scales separately.

Ferrofluids are magnetic liquids comprising magnetic nanoparticles (MNPs) dispersed in a non-volatile, non-magnetic fluid medium. Ferrofluids have been widely studied since the pioneering work of Rosensweig,<sup>8, 9</sup> where the so-called normal field instability in the presence of an external magnetic field gives rise to spectacular patterns of spikes. Ferrofluids find applications in magnetic resonance imaging,<sup>10</sup> hyperthermia treatment,<sup>11</sup> as host media for particle assembly,<sup>12</sup> and field-responsive composites.<sup>13</sup> More recently, magnetic fields have been used to manipulate ferrofluid droplet macro-patterns to make templates for micromolding microneedle arrays.<sup>14</sup> A comprehensive review highlights and evaluates the broadening applications of ferrofluids in fields as diverse as medicine, materials science, engineering, and the hard sciences.<sup>15</sup>

Research on ferrofluids has tended to focus on the macroscopic patterns that evolve when the magnetic nanoparticles (MNPs) that comprise the fluid respond to an applied magnetic field,<sup>16, 17</sup> or on electron microscope images of superparamagnetic nanoparticles in isolation from the

macroscopic spikes that might perhaps comprise them.<sup>18</sup> This is understandable because a challenge to linking the nano- to meso- to macro-scale patterns is the fact that conventional ferrofluids are dissipative systems. The characteristic spike patterns they produce when coupled to the magnetic field are not stable—they collapse when the field is removed. This makes it difficult to examine the ensemble of the spike patterns and the spikes, together with their underlying mesostructure. Thus in this respect, little is known about how the MNPs are organized within the spike structures, and what this organization might reveal about spike morphogenesis, and ultimately how spike morphogenesis might be linked to the macroscale patterns, and perhaps new functional properties. One way to prevent collapse is to "freeze" all elements of the patterns in place to obtain a type of "permanent recording" of the outcome of the magnetic field interaction. Of course, such a strategy is reminiscent of the recording of data bits in magnetic storage media, with the difference that one is interested not just in the "bits" but also how they are connected with the system-level architecture of the macro-pattern.

There have been several reports on the assembly of magnetic nanoparticles into permanent 3D structures. In this context, it is interesting to note that Velez et al. used magnetic pole patterns imprinted into magnetic tape to deposit 3D assemblies of MNPs into defined shapes.<sup>19</sup> After post-assembly multi-step chemical crosslinking, the shaped MNP assemblies retained their 3D geometry even after the field was removed. Jenus and Lisjak noted that randomly distributed, permanent ~ 500  $\mu$ m columnar structures of cobalt ferrite could be produced by evaporating water from citric acid stabilized charged MNP colloid pools in magnetic fields.<sup>20</sup> None of these studies on 3D assemblies explicitly explores mesoscale structure or the impact of the solvent host and/or chemical crosslinking on the normal magnetic field instability in magnetic fluids that can lead to

sudden symmetry breaking and the appearance of macro spike patterns at a surface, such as occurs in the Rosensweig regime.

In this Chapter, we report how solvent evaporation and irreversible polymer crosslinking yield permanent records of ordered patterns that emerge from magnetic field-directed assembly of MNPs in *volatile* ferrofluids. We reveal how order in the trapped structures spans the macroscale to the nanoscale and how these ordered patterns more universally resemble those observed in biological and geological systems. In our experiments, patterns are induced, and then sustained, by solvent evaporation and irreversible chemical reaction coupled with the complex ferrohydrodynamic response of the medium.

In the previous chapter, we used volatile alkane solvents to host MNPs. Because reaction-diffusion processes are known to play a fundamental role in pattern formation, we extend our analysis to a reaction-diffusion system comprising MNP/alkane solvent/alkoxysilane polycondensation. In this case, patterns are trapped by combining solvent loss with chemical crosslinking of the polymer network. New kinds of patterning and morphological detail emerge from this reaction-diffusion system. We therefore turn to electron microscopy to establish how spike patterns from both the alkane and alkane/polymer systems manifest additional texture and ranges of order at finer length scales. We show that the morphology of the patterns is sensitive to the relative humidity of the environment. In the closing section we give evidence of how our knowledge of the magnetic field response and ultrastructure of spikes can be used to make geometry-conserving solid-state transformations, converting magnetite nanocomposite spikes into complex iron oxides. Thus, because the magnetic field imposes orientational anisotropy on the trapped nanocomposite

structures, we can summon the memory of this orientational anisotropy to carry out a directed solid-state high temperature transformation of the magnetite nanocomposite. We demonstrate how kinetically trapped features in the spikes yield complex textured multilayered structures and encoded hierarchies of order from their antecedent ferrofluids. Our experiments and findings are discussed next.

## 4.3 Results and Discussion

The experiments described in Chapter 2 and 3 reflect patterning mediated by solvent evaporation and soft-soft interactions among ligands on the MNPs. Reaction–diffusion processes are known to be fundamental to pattern formation;<sup>21</sup> therefore, we extended our study to a reaction–diffusion system comprising MNP/alkane solvent/alkoxysilane condensation polymer. Polymers have in the past been used to stabilize 3D assemblies of MNPs.<sup>19</sup> From the literature, it is evident that incorporating MNPs directly into polymeric media is challenging because of the propensity of the nanoparticles to agglomerate.<sup>22</sup> In our hands, agglomeration can be avoided by hosting the nanoparticles in a low viscosity fluid organosilicon resin which can crosslink to form branching  $\equiv$ Si–O–Si $\equiv$  bonds by reaction with adventitious water vapor. This resin represents a reaction– diffusion system when combined with MNPs and coupled with an external magnetic field. In this case, patterns are trapped by combining solvent loss with silyl ether crosslinks. We selected a room temperature vulcanized (RTV) silicone host comprising methyltrimethoxysilane and a mixture of cage silsesquioxanes in mixed hydrocarbon solvents. When exposed to moisture, methyltrimethoxysilane rapidly hydrolyses and condenses with itself and with the silsesquioxanes to form a covalently crosslinked polymeric network. We find that new kinds of patterning and morphological detail emerge from this reaction–diffusion system.

#### 4.3.1 Trapped patterns from polymer ferrofluid in different alkanes

We use heptane, octane and nonane (C7-C9 alkanes) to deliver the MNPs. The starting composition of the ferrofluids contains 16.7 wt% RTV silicone. This value was determined by trial and error to ensure that the initial magnetization is below  $M_{\rm c}$ . For each composite ferrofluid, as the solvent evaporates, the magnetization similarly increases towards the threshold  $M_c$ . At a nominal field of 120 mT (dH/dz 16.2 mT/mm), the hexagonal phase emerges with no intervening square phase. Spikes form gradually and assemble into the nearly defect-free lattices shown in Figure 4.1A-C. The spike peak-to-peak distance  $\lambda$  increases with alkane chain length in the direction C7 to C9 diluent, i.e., in the same direction as surface tension  $\gamma$  increases (**Table 4.1**). The number of spikes N decreases as the wavelength  $\lambda$  increases. Figure 4.1D–E show that when H is increased to 160 mT (dH/dz 22.5 mT/mm),  $\lambda$  decreases for heptane and octane hosts. Interestingly, we observe no pattern at 160 mT for samples based on nonane, even though the applied H field is higher (Figure 4.1F). This is because the higher  $\gamma$  of nonane (compared with heptane and octane) and higher field gradient (compared with the field of 120 mT) raises  $M_c$  (see Equation 3.1), which now exceeds the magnetization of the sample during evaporation. We obtained a thin film of organized MNPs for this sample.



**Figure 4.1** Permanent patterns formed in a crosslinking polymer MNP composite ferrofluid diluted with different alkanes. The starting composition is: 5:5:2 (MNPs: alkane: polymer). A nominal field of 120 mT was used in (A) heptane (N = 110,  $\lambda = 1.24$  mm), (B) octane (N = 75,  $\lambda = 1.37$  mm) and (C) nonane (N = 30,  $\lambda = 1.42$  mm). A nominal field of 160 mT was used in (D) heptane (N = 170,  $\lambda = 1.03$  mm), (E) octane (N = 109,  $\lambda = 1.10$  mm) and (F) nonane. The scale bar is 2 mm. N is the number of spikes and  $\lambda$  is the peak-to-peak wavelength.

Alkane	Viscosity	Density	Vapor Pressure	Surface tension (liquid/air)	
	mPa s	g cm <sup>-3</sup>	(kPa@20°C)	$(mN m^{-1})$	
<i>n</i> -heptane	0.418	0.684	5.33	20.14	
<i>n</i> -octane	0.546	0.703	1.47	21.60	
<i>n</i> -nonane	0.713	0.718	0.341	22.85	

 Table 4.1 Selected physical properties of alkane solvents.<sup>23</sup>

## 4.3.2 Texture of spikes



**Figure 4.2** Morphogenetic outcomes of patterning of a conical spike from an evaporative ferrofluid. (A) SEM image of a typical spike derived from alkane-based ferrofluids. (B) Top view of a spike showing ring-like texture. (The tip is out of focus.) (C) High resolution SEM image of the spike surface showing the nanoscale ordering of the MNPs. Inset is the FFT image (processed by Image J) showing MNPs arranged in a rhombic lattice. SEM images of (D) A central spike and (E) A peripheral spike formed from the silicone/MNP evaporative ferrofluid composite. (F) A squamation pattern on the peripheral spike surface. Red triangle highlights in the insets locate the spikes with respect to the center of the hexagonal array in the sample.

The trapped patterns of spikes allow us to use electron microscopy to resolve their considerable morphological complexity over length scales spanning millimeters to nanometers. By scanning electron microscopy (SEM), conical spikes that emerge from alkane-based ferrofluids (described in Chapter 3) show what appear to be relatively smooth surfaces, regardless of their location within the hexagonal array. The spike tip in **Figure 4.2A** is typical of the morphology. It is capped with

a small dome that is punctured with holes on the order of 1  $\mu$ m. Longitudinal cracks radiate away from the tip. The spike appears to be assembled from rings or bands of material. These are visible as light and dark features circling the cone in **Figure 4.2A–B**. The micron-scale 3D ring pattern resembles Liesegang bands that arise in felsic volcanic rock, gels and precipitating salt media.<sup>24</sup> In the course of morphogenesis of the spike we ask, what is the morphogenetic outcome at the surface of the spike? **Figure 4.2C** resolves the nanoscale texture of the spike surface, where it is clear that the spherical nanoparticles assemble in a defected rhombic lattice (See inset Fourier transform of the real lattice pattern).

In addition, introduction of the crosslinking polymer leads to new kinds of patterning on the spike surfaces when compared with the alkane-only system. When we drive patterning of the silicone polymer/MNP composites, the surface texture of the spikes depends on the location of the spike with respect to the center of the pattern. This is because spikes evolve at different times during crosslinking/solvent loss. Spikes that evolve later grow under the influence of higher crosslink density, i.e. increased viscosity. The central spike represented in **Figure 4.2D** is first to form. Viewed from the top, its relatively smooth surface exhibits radial bands of elongated holes (see inset in **Figure 4.2D**). **Figure 4.2E** shows a spike located at the outer perimeter of the array. The surface of the cone is textured in a way that resembles anisotropic Voronoi squamation (patterns of scales in fish). The tiling is populated with patterns of holes (**Figure 4.2F**). These holes are likely vents that allow solvent evaporation. The morphogensis of the polymer spikes can be attributed to the reaction of polymerization coupled with the diffusion of MNPs throughout pattern formation. Therefore, adjusting the ratio of the reaction/diffusion components in the system may lead to new types of patterning.

#### 4.3.3 A mixed hexagonal and labyrinthine pattern

Indeed, a new kind of patterning emerges when a ferrofluid contains additional polymer above 16.7 wt%. Figure 4.3A shows that the pattern consists of coexisting hexagonal and labyrinthine phases derived from a ferrofluid with 25 wt% RTV silicone in a 120 mT field (dH/dz 16.2 mT/mm). Spikes in the hexagonal lattice (Figure 4.3C) emerge early in the pattern. The hexagonal lattice shifts off the center to the left. This asymmetry may be due to experimental artifacts, possibly the ferrofluid was not homogeneous in the mixing step. The surfaces of all the spikes are tiled similarly to those shown in Figure 4.3E. As polymerization proceeds, the crosslinked host hinders the diffusion and assembly of MNPs to make new spikes. Instead, the MNP composite evolves into a labyrinth. The base of the spikes and the coastline of the labyrinth deserve scrutiny. These regions consist of palisades of "fibers" that rise almost vertically from the substrate. This is most evident in Figure 4.3B which shows a close-up of a "fjord" in the surrounding labyrinth landscape. High aspect ratio fiber-like features are clearly discernable. They are similar in size, measuring  $\sim 500 \,\mu\text{m}$  in length and 20–25  $\mu\text{m}$  in width. They are stacked together in columnar joints and lean away from the exposed face of the involution. The structures call to mind columnar jointing that occurs when lava slowly cools and cracks into hexagonal pillars of basalt, as seen in the spectacular patterns near Fingal's cave on Staffa, Scotland. Moving "inland", the fiber-like structures become embedded in a homogeneous matrix that is visible as dark contrast in the SEM image. The tops of the fibers emerge as white highlights in the image. Figure 4.3D shows a collection of the fiber-like features protruding from the undifferentiated matrix. Viewed from above, they approximately define a distorted and defected rhombic lattice. The protrusions are decorated with one, two or three holes/indentations that measure about 5  $\mu$ m. The overall pattern is asymmetric, probably due to uneven mixing. If we further increase the polymer content
to 50 wt%, the pattern becomes a full labyrinth, resembling what is classically observed in thin ferrofluid films in a Hele-Shaw cell (**Figure 4.4**).<sup>25, 26</sup> The impact of increasing polymer content in ferrofluid formulation on macro pattern formation is similar to that of OA described in Chapter 3.



**Figure 4.3** A coexisting hexagonal-labyrinthine pattern. The starting composition is 1:2:1 (MNP: nonane: prepolymer). (A) Optical micrograph of the pattern. SEM image of (B) the labyrinthine region showing fiber-like structures, on which stands (C) a hexagonal array of spikes and (D) a pattern of relief texture (white highlights) embedded in a dark background matrix. Inset shows a relief texture protrusion with two holes or indentations.



Figure 4.4 A full labyrinthine pattern derived from a nonane ferrofluid with 50wt% silicone polymer.

## 4.3.4 Humidity control on pattern formation

Earlier in the chapter we explained how an RTV silicone prepolymer can be viewed as a reactiondiffusion system to investigate the effects of this system's properties on pattern formation in a magnetic field. Methyltrimethoxysilane in the prepolymer formulation reacts with water to release methanol and promotes nucleophilic attack by silanol on nearby silicon alkoxide and other silanol species to crosslink the polymer through polycondensation reactions. We were therefore motivated to investigate how humidity as a control variable impacts pattern formation in the evaporating ferrofluid formulation.

We adopt the setup of Park and Kim to create a controlled humidified environment.<sup>27</sup> Figure 4.5 illustrates a beaker of hot water heated on a hotplate and placed in a sealed plexiglass chamber. The humidity is controlled by the temperature and monitored by a hygrometer. The ferrofluid sample was allowed to evaporate within the enclosure. In this setup, video recording is not possible because of the high humidity. The samples were left inside the chamber for 3 hours to ensure

complete evaporation and polymerization. After that, the samples were retrieved and left to dry overnight. We analyzed the resulting patterns by electron microscopy and optical microscopy.

We used one-part silicone prepolymer to three-parts 33wt% ferrofluid. Initially, we set the relative humidity (RH) to 60%. The magnetic field strength was fixed at 120 mT. The pattern that evolved exhibits a morphology similar to that obtained under 40% RH (compared to **Figure 4.3**). **Figure 4.6A** shows an aerial view of the pattern obtained under 60% RH. While it resembles the mixed hexagonal-labyrinthine pattern seen in **Figure 4.3**, there are differences due to the increased water content in the chamber.



Figure 4.5 Schematic setup for humidity-controlled experiment.

We analyze the entire pattern according to three distinct regions: spikes, sheets and rings. The latter two structures are new compared to the classic Rosensweig spike pattern. A central hexagonal lattice of spikes is obvious (**Figure 4.6B**). Circular cracks are visible at the base of the spikes. Under SEM magnification, the spike tip surface appears lightly textured with flow lines and decorated with occasional vent holes (close-up, **Figure 4.6D**). The spikes emerge from a

network or wrinkle pattern of bridges in the plane of the substrate that on close inspection comprise the palisade sheets of fiber-like structures seen in **Figure 4.3**. Rising from the substrate floor, the bridge architecture culminates in ramifying knife-edge ridges, all of which are assembled from the fibers. This is evident in **Figure 4.6C**. Given our analyses thus far, it seems likely that the fiber texture results from the magnetic field response of the thinning inter-spike film and the competition among material flow patterns that arise during the birth and growth of spikes. We suggest that the fibers arise from orientated side-by-side aggregates of chains of magnetite nanoparticles.

The morphology of our 2D fiber sheets resembles those of Yin et al. who reported assembling large >100 nm Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles in a magnetic field.<sup>28</sup> (In their experiment, they oriented the core-shell magnetite nanoparticles by magnetic field into palisade-like sheets on photolithographically patterned substrates between parallel glass windows and then fixed the resulting structures in place by infusions of polyurethane.) In **Figure 4.6E** the palisade texture we observe for our system extends into the labyrinth-like wrinkle pattern at the outer edge of the interior spike pattern before transitioning to the continuous dark ring visible at the interface with the green annular disk (The green coloration was digitally superimposed to clarify the boundary region.). In **Figure 4.6E** the sheet fibers are tilted in the direction of the flow field, which is toward the center of the sample. The right-hand side section of **Figure 4.6E** is the interior edge of the green ring adjacent to the wrinkle pattern. An enlargement of this area is captured in **Figure 4.6F** where it evidences protrusions similar to those recorded in **Figure 4.3**. In the present instance, we identify two populations of protrusions with diameters of ~ 0.3 µm and ~1.5 µm. The protrusions are the tips of the fiber bundles.



**Figure 4.6** (A) The macroscopic pattern formed under 60% RH from RTV silicone polymer-based ferrofluid. The ring area is digitally colored green. The different regions are (B) seven spikes in a hexagonal lattice (C) sheet-like columnar structures (D) spike surface (E) assemblage of columnar sheets into a knife-edge ridge leading to a spike base (F) two populations of protrusions in the ring area near the edge.

The experiment was then conducted with a fresh sample under 70% RH. The results are shown in Figure 4.7A. The central hexagonal pattern is present, but the surface of the spikes is more textured than that prepared at 60% RH. This is traced in successive enlargements in Figure 4.7C, D and F with different z-axis focus. Figure 4.7C gives a top-to-bottom view of the patterns on the surface of the spike from the tip to the base where the spike yields to rather coarse decoration. At the top of Figure 4.7D the flow line is left-handed chiral, spiralling upward to the apex of the spike. Hole patterns are visible, which can be used to trace the upward climb of the texture. The holes taper in the direction of the upward twist. At the apex, there are two large holes and evidence that the smaller holes are aligned along flow lines that are separated into periodic troughs nearby. Figure 4.7E shows that the base comprises sheets of columnar structures that sweep up into the spike from the substrate floor. A knife-edge ridge of material can be seen feeding the spike base from the center left side of the image. Figure 4.7F provides a striking perspective of the different length scales and periodicity of the surface texture on the spike. Viewed from the top, we observe a series of concentric bands descending in a series of rings from the cone apex. The relatively smooth texture of the cone tip yields first to a girdle band of webbed openings. Below it are bands consisting of a latticework of vertically aligned periodically patterned slotted holes.

Turning our attention to the outer ring territory in **Figure 4.7G**, we again detect the sheet-like structures observed in patterns that emerged at 60% RH. In the ring area, we observe a transition from what appears to be "dots" to "lines". The "dots" correspond to the protrusions described in **Figure 4.6**. The "lines" distributed radially at the edge may correspond to column elements that make up the sheet-like structures near the edge (**Figure 4.7G–H**).



**Figure 4.7** (A) The macroscopic pattern produced under 70% RH from RTV silicone polymerbased ferrofluid. (B) seven spikes in a hexagonal lattice; (C) tip of a spike; (D) a spike of interest; (E) bands of holes on the spike surface; (F) sheet structures near the base of the spike; (G) the ring area showing a transition of texture from "dots" to "lines" with magnification in (H).

The hexagonal phase spike pattern is suppressed when the relative humidity reaches 80%. At this stage, the whole pattern in **Figure 4.8A** is separated into domains that are poorly visible at low magnification. Spikes in **Figure 4.8B** have transformed into perforated conical frustums. The sheet-like columnar structures are no longer observed. **Figure 4.8C** shows an edge of the dark outer ring area on the right in the optical micrograph. The surface is textured with protrusions with diameter ~10  $\mu$ m. In successive magnifications in **Figure 4.8D**–F, we observe remarkable populations of flat-topped rounded rectangles (stadiums) and ovals, with one or two center holes, fused in defected square arrays (**Figure 4.8F**). These surface geometries result from the coalescence of micron-sized fibers. In **Figure 4.8E**, the arrow points to collections of the fibers that, from left to right, fuse to make a vertical mass that flows into finger pattern convolutions.

The morphology we observe so far is reminiscent of the *Breath Figure* (BF) pattern, which was first studied over 100 years ago.<sup>29</sup> The BF pattern is generated conventionally by evaporating a solution of polymer on a solid substrate in a humid environment. This is similar to our experimental configuration where we evaporate our polymer-based ferrofluid in a humid chamber. The mechanism for BF pattern formation has not been fully comprehended because it involves complicated non-equilibrium heat and mass transfer. But the general idea behind BF formation is understood as follows. When solvent evaporates, the temperature at the liquid/air interface decreases due to the latent heat of evaporation. Water vapor then condenses on the solution surface. The condensed water droplets grow and self-assemble into an ordered array. This array of water droplets determines the final structure of the dried polymer. Eventually the solvent and water evaporate completely, leaving a patterned array of polymer structures. We suggest that such a process may be at work in the morphogenesis of hole patterns in our ferrofluid systems. Future

work on fine tuning our experimental conditions may shed light on the mechanism of the formation of column structures and their assembly into more complex patterns.



**Figure 4.8** (A) Visible light micrograph of macroscopic pattern formed under 80% RH from RTV silicone polymer-based ferrofluid. (B) a perforated conical frustum; (C) holes near the dark the ring area; (D) transition from ring area on the left to a conical frustum on the right; (E) tube-like structures and curved fingering structures; (F) the upper side of the tubes showing one or two holes.

### 4.3.5 Solid state transformation of spikes

Having induced and captured periodic, orientational and magnetic field anisotropy in our materials, it remains to determine if some memory of this anisotropy can be transferred from the magnetite nanocomposite template to a new product by thermal transformation. To show this, we heat samples of alkane-derived spikes in a tube furnace in air and under argon (Figure 4.9A). The purpose was to determine how the sample transformed in an oxidizing atmosphere compared with an inert atmosphere. Spikes heated at 800 °C in air present smooth surfaces and retain the spike geometry, but the cracking patterns point to an underlying orientational anisotropy conferred by the response of the original MNP system to the magnetic field. In Figure 4.9B we observe that thermally treated spikes fracture longitudinally and radially, cleaving into several parts; ring fractures are evident in the basal view. Cleavage planes are sharp, suggesting that cracks propagate along a path of least resistance, most likely created by alignment of MNPs. The crack patterns correspond to tensile stress relief typical of Mode I fracture.<sup>30</sup> The pattern of these fractures is reminiscent of the stress relief response during desiccation of the vascular tissues of tree rings. The ring fractures prefigure a surprising outcome when spikes are heated to 800 °C under argon. It is known that the magnetite nanoparticles can react with carbon from the decomposition of the organic oleic acid under high temperature.<sup>31</sup> Figure 4.9C shows the skin of one of the many spikes that reveal textured multilayers. These skins feature polygonal crystals and occasional vertical plates of hematite, identified by confocal Raman spectroscopy (Figure S4.3). The cross-section of the skin consists of two layers, each about 5  $\mu$ m thick, with a visible interface between them. The cleavage facet consists of vertical columns that run roughly orthogonal to the sheet curvature.



**Figure 4.9** Ultrastructure of thermally transformed spikes from alkane-based ferrofluids. (A) Spikes comprising MNPs heated under different atmospheres undergo either oxidation or reduction reactions to yield oriented bulk-phase iron oxides. SEM images of (B) samples heated at 800°C in air showing longitudinal crack, circular crack and circular fragmentation at the base. SEM images of (C) samples heated at 800°C under argon showing the multiple-layer structures. The outermost "bilayer" is decorated with needle- and plate-like hematite crystals.

We observe similar cracking patterns and multilayer textures when the RTV silicone polymerdoped counterparts (**Figure 4.10**) are heated in air and argon. We note that when control samples of MNPs, not exposed to a magnetic field, are heated to 800 °C, they convert to randomly oriented crystallites. The unique morphology shown in **Figure 4.9C** is likely a reflection of the layer-bylayer lattice arrangement of the nanoparticles in the spike. This is in line with the SEM images observed above in **Figure 4.2C** for example. In summary, tracing the lineage of this thermal transformation, we began with uncorrelated magnetic nanoscale particles. Self-organization of MNPs yielded a macro-pattern that is permanently trapped as an assembly of spikes. The macroscale spikes encode hierarchies of order, texture and anisotropic orientational and magnetic properties that condition the products of their thermal transformation. Given the versatility in formulating and doping ferrofluid compositions, this solid-state experiment is intended to invite others to confer additional functionality on nanocomposites by combining order-conserving transformations with addition of new properties by adventitious doping.



**Figure 4.10** A silicone-doped spike transformed at 800°C (A) in air and (B) under argon. Inset shows the corresponding optical micrograph.

# 4.4 Conclusion

In conclusion, this study provides new insight into how trapping of magnetic field-directed assembly of magnetic nanoparticle composites leads to hierarchies of patterning that conserve features of the underlying magnetic and structural anisotropy. The kinetically trapped state can be traced back to its antecedent ferrofluid pattern. We show that pattern formation and morphological ultrastructure over many length scales depend sensitively on ferrofluid composition and the complex interplay of magnetic field, solvent evaporation, chemical reaction and MNP interactions. The possibility of designing hierarchically structured matter from magnetic fluids is demonstrated by a directed solid-state transformation of the MNP composite spike to a new product that encodes the structural complexity of the trapped state.

## 4.5 Materials and Method

### 4.5.1 Materials

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were synthesized by thermal decomposition as described in Chapter 3. RTV silicone resin (DOWSIL<sup>™</sup> 1-2620) was purchased from Dow Corning. All other chemicals were purchased from Sigma-Aldrich.

## 4.5.2 Humidity control

The dimensions of the chamber are  $1 \text{ m} \times 1 \text{ m} \times 1 \text{ m}$ . A 2-liter beaker with 1.6 L of deionized water was heated to 80 °C, 85 °C or 90 °C for a relative humidity of 60%, 70% or 80% in the chamber. Note that this value may vary for different hotplates.

## 4.5.3 Preparation of ferrofluids and patterning

Dried Fe<sub>3</sub>O<sub>4</sub> nanoparticles (100 mg) were dispersed in an alkane (100 mg of heptane, octane or nonane). The resulting homogeneous mixtures are referred as alkane-based ferrofluids. To make crosslinking ferrofluids, RTV silicone resin (DOWSIL<sup>TM</sup> 1-2620, 40 mg) was added dropwise to an alkane-based ferrofluid (200 mg, 50 wt%). The suspension was thoroughly mixed until homogenous with a vortex mixer. The as-prepared ferrofluid (200 mg) was deposited into a polystyrene petri dish (Corning, Falcon Dish 35×10 mm Easy Grip) where it coated the bottom surface. The sample was then placed above a 25.6×9.5 mm NdFeB permanent disk magnet (DX06-N52, K&J Magnetics) at a distance of to yield a nominal field of 120 mT. The distance between the sample and the magnet was controlled by a linear translation stage. The sample was allowed to evaporate. Images and videos were obtained during various stages of solvent evaporation.

### 4.5.4 Thermal solid-state transformation of MNP-assembled spikes

As-assembled spikes extracted from the central portion of the hexagonal pattern were heated at 5 °C/min to 800 °C in a quartz lined tube furnace (Lindberg/Blue, Thermo Scientific) under air or argon and held for 3h, after which time the sample was ramped down at 5 °C/min to room temperature.

### 4.5.5 Characterization

Nanoparticles were imaged with a Philips CM200 transmission electron microscope (TEM) at 200 kV. Permanent spikes were imaged by an FEI Inspect<sup>™</sup> F50 scanning electron microscope (SEM) or an FEI Quanta 450 Environmental Scanning Electron Microscope (FE-ESEM). Optical images and videos were acquired by a Thorlabs Compact USB 2.0 CMOS Camera mounted on an AMG optical microscope and a Keyence VHX-7000 Digital Microscope. Magnetic properties of MNPs were measured using a SQUID magnetometer (MPMS 3 XL, Quantum Design). Magnetization curves were obtained over a range from -7 T to 7 T.

# 4.6 Supporting information

### 4.6.1 Characterizations of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The oleic acid capped Fe<sub>3</sub>O<sub>4</sub> nanoparticles have an average diameter of 15 nm (Figure S1A). Superconducting quantum interference device (SQUID) magnetometry shows that the MNPs are superparamagnetic and have a saturation magnetization of 69.3 emu/g at room temperature (Figure S1B). The surface ligands of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were characterized by FT-IR to confirm that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were coated with oleic acid (Figure S2). We assign peaks characteristic of OA bound to the iron oxide surface as follows: Symmetric and asymmetric stretching of CH<sub>2</sub> is observed at 2852 and 2916 cm<sup>-1</sup>. The C=O stretching mode of neat OA at 1714 cm<sup>-1</sup> is replaced by two symmetric and asymmetric COO<sup>-</sup> stretches at 1432 and 1523 cm<sup>-1</sup> can be identified as the bounded ligand. The Fe-O stretching is observed at 626 cm<sup>-1</sup>.



**Figure S4.1** SQUID magnetometry of 15 nm magnetite MNPs. (A) TEM image of as-synthesized magnetite MNPs. The inset is high resolution image of the spherical magnetite nanoparticles. (B) Hysteresis loop of powdered magnetite MNPs at room temperature.



Figure S4.2 Infrared spectra of neat oleic acid (OA) and OA coated magnetite nanoparticles.

## 4.6.2 Additional data



Figure S4.3 Raman spectra of a spike transformed from magnetite to hematite at 800°C (in air or under argon). In both cases, peaks characteristic of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) are observed at 223 cm<sup>-1</sup>, 288 cm<sup>-1</sup>, 408 cm<sup>-1</sup>, 610 cm<sup>-1</sup> and 1321 cm<sup>-1</sup>.<sup>32</sup>

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# Chapter 5 Ferromagnetic Resonance of Self-Organized Spike Superstructures of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles

## 5.1 Abstract

Self-organization of magnetic nanoparticles (MNPs) may give rise to superstructures with collective properties that differ from individual nanoparticles. Characterization of the self-organized structures is of fundamental interest to understand the nature of the collective properties. Here, we report the use of ferromagnetic resonance (FMR) to probe the magnetic properties of spike superstructures of MNPs resulting from self-organization of spherical, cubic and polydisperse MNPs. We first analyze the FMR resonance field and the linewidth for non-interacting MNPs in dilute ferrofluids. From the linewidth we quantify the anisotropy constant  $K_1$  for non-interacting spherical, cubic and polydisperse MNPs to be 9.74 kJ/m<sup>3</sup>, 5.44 kJ/m<sup>3</sup>, and 8.41 kJ/m<sup>3</sup>, respectively. We then explore the spike superstructures comprising interacting MNPs. The spikes exhibit uniaxial anisotropy in their angle dependent FMR response. The temperature dependent FMR signals of the spike superstructures are typical of superparamagnetic MNP systems. Dipole-dipole interaction contributes to the shift of resonance field and change in the linewidth for spike superstructures of interacting MNPs. We suggest that the spike superstructures exhibit superferromagnetic behaviors.

# 5.2 Introduction

Self-organized structures of magnetic nanoparticles (MNPs) show collective properties that differ from the magnetic properties inherent in their isolated or non-interacting MNP constituents. For example, the superspin glass (SSG) and superferromagnetic (SFM) states show collective magnetic properties that arise from strong interparticle interactions of superparamagnetic nanoparticles in self-organized structures.<sup>1</sup> The SSG state is a magnetic super-phase that occurs in strongly interacting MNP systems. It refers to the disordered orientation of the superparamagnetic spins, similar to the spin glass state in crystals. The SFM state can be understood as the counterpart of ferromagnetism in ensembles of superparamagnetic MNPs. Interparticle interactions are of two origins depending on interparticle distance: exchange interactions and dipole-dipole interactions. Previously, we showed that magnetite nanoparticles self-organize into patterned millimeter-sized conical spikes and labyrinths. Spikes were obtained by evaporation of volatile ferrofluids in the regime of the Rosensweig instability. Conical spikes are in essence superstructures of magnetite nanoparticles. We have imaged the organized spike structures of MNPs by electron microscopy, but we have little information about their collective magnetic properties.

Ferromagnetic resonance (FMR) is widely used to explore magnetic properties of magnetic materials and its broad application has been reviewed by Furdyna and Liu.<sup>2</sup> As introduced in Chapter 1, the nanosecond resolution of FMR makes it suitable for studying time-dependent magnetic properties of MNP systems, like barriers to spin thermalization that are much shorter than the time scale of common magnetometry. Ferromagnetic resonance can distinguish (1) a narrow range of particle size and shape; (2) chain structure; and (3) crystal elongation.<sup>3</sup> The

archetypal structure of interacting MNP systems is the head-to-tail chain. Zhai et al. studied the FMR response of chains of 150 nm magnetite (Fe<sub>3</sub>O<sub>4</sub>) particles. The signals were well-fitted by including effects of shape anisotropy and demagnetization factors.<sup>4</sup> The FMR response of chains of 150 nm particles can be modeled with the bulk shape anisotropy of magnetite since this particle size manifests properties similar to the bulk phase.<sup>5</sup> Elsewhere, experimental and numerical studies on chains of magnetite nanoparticles, average nanoparticle size ~35 nm, in magnetotactic bacteria showed a characteristic anisotropic and multi-peak FMR spectral response.<sup>6-8</sup>

Interpretation of more complex 3D superstructures of interacting MNPs by FMR remains a formidable challenge. In part, this is because the FMR spectra of interacting MNPs show asymmetric lineshape with a rather large linewidth. The resonance fields shift with different quantities of solids, which makes it challenging to reproduce and interpret the FMR spectra of MNP solid samples. Moreover, determination of magnetic parameters from spectral features can be compromised by heterogeneity in the particle size distribution that is convolved with the magnetic response. FMR spectral characteristics like effective g value ( $g_{eff}$ ), full width at half maximum in lineshape, and linewidth for symmetric Gaussian broadening are usually determined with empirical parameters. These empirical parameters differ from the physical parameters that control the spectral response viz., g value, the effective anisotropy field, magnetocrystalline anisotropy and Gaussian broadening.

As mentioned above, advances in FMR theory and experiments have been hampered by sample and particle shape polydispersity. To date, we observe that many of the highly cited FMR experiments on MNPs and their assemblies have been conducted on MNP samples that were polydisperse in size and shape.<sup>9-12</sup> Use of monodisperse nanoparticles can significantly simplify efforts to distinguish intrinsic intraparticle effects from interparticle interactions by theory and experiment. Only recently has the FMR response of non-interacting monodisperse MNPs been reported.<sup>13-15</sup> In this Chapter, we explore the FMR response of monodisperse magnetite nanoparticles both in colloidal suspension and as self-organized solids. From FMR spectra and magnetometry, we probe the magnetic anisotropy of the conical spikes and structural information of the self-organized MNPs. In addition, we compare the FMR response of monodisperse spherical and cubic MNPs with that of polydisperse MNPs, in both non-interacting and interacting systems. Our results and findings are discussed below.

# 5.3 Experimental

### 5.3.1 Sample preparation

Monodisperse spherical and cubic magnetite nanoparticles were synthesized by thermal decomposition of iron oleate as described in Chapter 3. Polydisperse magnetite nanoparticles were prepared by coprecipitation as described in Chapter 2. For FMR measurements of ferrofluids, MNPs were first dispersed in octane to a concentration of 25 wt%. Additional octane was added to dilute the ferrofluid to the desired concentration to evaluate the concentration dependence of the FMR measurements. To prepare samples of spikes for FMR, sphere, cube and polydisperse MNPs were dispersed in octane to 25 wt%. The standard pattern formation process described in Chapter 2 was used to elicit trapped spikes from the ferrofluid formulations. Spikes were extracted from the central part of the resulting patterns for FMR analysis.

### 5.3.2 Ferromagnetic resonance measurement

Careful handling of solid samples is needed to ensure reproducibility of the FMR signals. A spike of interest was glued (cyanoacrylate, Super Glue<sup>®</sup>) to a capillary glass tube perpendicular to the long axis of the tube. The assemblage was then inserted into a standard EPR fused silica tube. Like the EPR tube, the glass capillary tube is EPR silent under all experimental conditions. FMR spectra were measured with a Bruker Elexsys E580 X-band EPR Spectrometer. The EPR spectrometer was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH) with a *g* value of 2.0036. The acquisition parameters were as follows: sweep field width 600 mT, modulation frequency 100 kHz, modulation amplitude 0.1 mT, microwave power 35 dB, time constant 1.28 s, conversion time 20.48 s.

Angle-dependent measurements were carried out in the cavity equipped with a goniometer. **Figure 5.1** illustrates how a spike sample is oriented parallelly to the electromagnet in the spectrometer. This setup allowed the sample to be rotated with respect to the homogeneous magnetic field in the cavity. Temperature-dependent measurements were conducted for the field aligned parallel and perpendicular to the sample. A continuous-flow nitrogen cryostat was used to adjust the temperature from 120 to 290 K.



**Figure 5.1** Schematic of orientation of a conical spike parallel to the magnetic field (blue dotted lines) in the microwave cavity of the spectrometer. The spike can be rotated with a goniometer inside the cavity to study the angle-dependent response to the magnetic field.

## 5.3.3 SQUID magnetometry

Magnetization hysteresis loops were recorded at 300 K using a Quantum Design SQUID-VSM MPMS from -7 T to 7 T. Zero-field-cooling/field-cooling (ZFC/FC) curves were obtained from 3 K to 300 K. In ZFC measurements, the samples were cooled from 300 K to 3 K in the absence of an external field. At 3 K, a field of 100 Oe (10 mT) was applied and the magnetization was recorded as the temperature increased. For FC experiments, the samples were cooled from 300 K under an applied field of 100 Oe (10 mT); then the magnetization was recorded as the temperature increased.

# 5.4 Results and Discussion

Ferromagnetic resonance spectra of MNP systems typically show a broad absorption across a few hundred milli-Tesla (mT). The resonance field and the lineshape depend sensitively on the magnetic properties of the magnetic nanoparticles, e.g. saturation magnetization, intrinsic magnetocrystalline anisotropy, dipole-dipole interactions, shape anisotropy. FMR spectra are generally characterized by two parameters: the resonance field  $H_{res}$ , defined as the zero-crossing point of the FMR curve, and the linewidth  $\Delta H_{pp}$ , defined as the peak-to-peak distance between the maximum and minimum of the FMR curve. The g value is related to the resonance field according to  $g = h\nu/\beta H_{res}$ , where h is Planck's constant, v is the microwave frequency, and  $\beta$  is the Bohr magneton. It should be mentioned that the g-value in FMR is actually an *effective* g-value, geff, which deviates from the classic Landé g-factor g, which has all the anisotropy factors of the magnetic nanoparticle removed. The deviation from  $g \approx 2$  depends on the local environment of the spin or the "macrospin" in MNPs, and fundamentally the spin-orbit interaction. If MNPs aggregate or interact, then one would expect a change in the local environment of the macrospin and therefore a shift in  $g_{eff}$  value. In the next section, we demonstrate the dependence of the resonance field  $H_{res}$ on MNP concentration in FMR.

## 5.4.1 FMR spectra of ferrofluids

First, we examine the FMR response of ferrofluids. **Figure 5.2** shows the FMR spectra of a ferrofluid consisting of spherical MNPs in octane at different wt% concentrations. The concentration, *c*, of the ferrofluid was lowered by dilution with the octane solvent. The FMR lineshape is asymmetric, exhibiting a broad low field band and a sharp high field band. This two-peak absorption feature resembles the FMR lineshape interpreted for ferrofluids derived by

Raikher and Stepanov.<sup>12</sup> According to their analysis, the two peak spectrum is due to competition between effects due to thermal fluctuations (barrier to thermalization of superparamagnetic spins) and changes in the orientational distribution (function) of the ensemble of nanoparticle axes of magnetic anisotropy. The latter depends on the orientational mobility of MNPs whose magnetic anisotropy axes change under the influence of the applied field. The competition between the two contributions is temperature dependent.



Figure 5.2 Ferromagnetic resonance of ferrofluids comprising spherical MNPs in octane. Variation of FMR spectra with concentration (by weight%). Red dots indicate the positions of the resonance field ( $H_{res}$ ).

In **Figure 5.2** we observe that  $H_{res}$  shifts towards a lower field with dilution. The shift is indicated by the positions of the red dots on the curves. At a sufficiently low concentration, the resonance field remains unchanged at 283 mT (g = 2.35) with further dilution. In this low concentration regime, interparticle magnetic dipole-dipole interactions are suppressed due to the large separation between the MNPs. Below 0.1 wt%, the sharp high field peak diminishes. The resulting FMR lineshape is Lorentzian.

For ferrofluids with  $c \ge 1.62$  wt%, the FMR signals show a distinctive two-peak absorption that can be described by an axial g value, where  $g_x = g_y \neq g_z$ . As the concentration increases, the highfield peak shifts to even higher field but the low-field peak does not change position with concentration. Concomitantly, the overall peak-to-peak linewidth  $\Delta H_{pp}$  increases. Based on the axial g anisotropy, the physical origin of this unique lineshape is most likely linked to chain formation in concentrated ferrofluids. It is reasonable to assume that dipole-dipole interactions among the MNPs are enhanced, assisted by the homogeneous magnetic field in the cavity. Chains produced in this way will exhibit shape anisotropy expressed through the demagnetization field  $H_d = \mu_0 (N_z - N_z) M_s$ , where  $\mu_0$  is vacuum permeability,  $N_z$  and  $N_x$  are the demagnetization factors in z and x directions and  $M_s$  is saturation magnetization. It is well-known that the average number of particles in chains is proportional to the concentration.<sup>16-18</sup> Similar to Zhai et al.,<sup>4</sup> the longer the chain, the higher the average number of particles. This causes a higher  $N_z$ - $N_x$ , increasing the demagnetization field  $H_d$  that shifts the resonance field and broadens the linewidth. This is also confirmed by Marin's study, where FMR simulations based on particle-particle 1D chain formation showed that the linewidth increases with increasing concentration in ferrofluids.<sup>19</sup> The FMR lineshape therefore responds to changes in the internal structure of ferrofluids in a magnetic field. For lower concentrations, the FMR spectra become symmetric. We will discuss them in detail later.

### 5.4.2 FMR spectra of aggregating MNPs in octane over time

In order to understand how MNP aggregation affects the FMR lineshape, we prepared a ferrofluid in octane that is unstable in an external applied magnetic field, but stable in its absence. For such a sample, MNPs agglomerate slowly when the magnetic field is applied. Particle aggregation was promoted by removing ligand from the surface of the MNPs so that steric stabilization was diminished. This was done by washing the nanoparticles with methanol. Agglomerates are visible as dark precipitates in a lightly brown ferrofluid supernatant.



**Figure 5.3** Time-dependence FMR of lineshape of an unstable ferrofluid showing a shift in the low field  $H_{\text{res}}$  from 267 mT to 252 mT and an increase of the linewidth from 130 mT to 135 mT.

**Figure 5.3** shows the FMR spectra of a 0.1 wt% MNP ferrofluid over a period of 13 min. MNPs in the ferrofluid start to agglomerate as soon as the field is turned on. Note that the resonance field at the starting point shifts from 283 mT, the value for non-interacting spherical MNPs, to 267 mT. This indicates that MNPs interact with among themselves in the absence of an applied magnetic

field. The resonance shifts to lower field and the peak-to-peak linewidth  $\Delta H_{pp}$  broadens and intensifies. From **Figure 5.3**, the broadening is associated with shifts to lower field of the low field peak. The high field peak position remains unchanged. When the field is turned off, the precipitate can be redispersed by sonication. A rapid scan of the FMR response of redispersed precipitate shows that it is identical to the original spectrum at time 0 s.

5.4.3 Characterization of sphere, cube, and polydisperse MNPs



**Figure 5.4** TEM micrographs of (A) 14.8 nm spheres (B) 10.0 nm cubes (C) 9.18 nm polydisperse MNPs. Insets show lattice features of the high-resolution images of the sphere, cube and polydisperse MNPs.

Here we synthesize MNPs with three different shape profiles: monodisperse spheres, monodisperse cubes and nanoparticles that are polydisperse in shape and size distribution. We shall refer to them as sphere, cube and poly MNPs. By transmission electron microscopy (TEM), we can image the size and shape. The sphere MNPs have an average diameter of 14.8 nm (polydispersity index (PDI) =  $\sigma/\bar{d} = 0.0066$ ). The cube MNPs have an average side length of 10.0 nm (PDI = 0.0101). The poly MNPs have an average diameter of 9.18 nm (PDI = 0.022). Size

distribution of these MNPs can be found in Section 5.6.1. Approximating the volume of a particle drawn from the poly MNPs based on a sphere with a 9.18 nm diameter, we have the following volume order:  $V_{\text{sphere}} > V_{\text{cube}} > V_{\text{poly}}$ .

#### SQUID magnetometry of sphere, cube and poly MNPs

Magnetic properties of MNPs in the solid state were determined by SQUID magnetometry. The hysteresis loops of the three MNPs in powder sample are shown in **Figure 5.5A**. The saturation magnetizations  $M_s$  measured at 300 K are 69.0 emu/g, 73.1 emu/g, and 73.3 emu/g for the sphere, cube and poly MNPs, respectively. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves for the powder MNPs are presented in **Figure 5.5B**.



**Figure 5.5** SQUID magnetometry of the sphere, cube and poly MNPs. (A) room temperature hysteresis loops (B) Field-cooled/zero-field-cooled (FC/ZFC) magnetization curves.

The blocking temperature  $T_{\rm B}$  was extracted from the maximum of the ZFC curves.<sup>20</sup> The blocking temperatures  $T_{\rm B}$  of the sphere, cube and poly MNPs are 256 K, 214 K, and 210 K, respectively. The anisotropy constant  $K_{\rm eff}$  is given by<sup>21</sup>

$$K_{eff} = \frac{T_B k_B \ln({}^{t_m}/\tau_0)}{V}$$
(5.1)

where  $T_B$  is the blocking temperature,  $k_B$  is the Boltzmann constant, V is the particle volume,  $\tau_m$  is the measurement time and  $\tau_0$  is the Néel characteristic time. The term  $\ln(\tau_m/\tau_0)$  is ~25.3 for standard SQUID experiments ( $\tau_m \sim 10$  s and  $\tau_0 \sim 10^{-10}$  s).<sup>21</sup> From these parameters we calculate the respective anisotropy constants  $K_{eff}$  for sphere, cube and poly MNPs which are 52.7 kJ m<sup>-3</sup>, 74.7 kJ m<sup>-3</sup> and 181.0 kJ m<sup>-3</sup>. The exceptionally large  $K_{eff}$  value for poly MNPs is probably due to the inaccurate representation of the particle volume polydispersity through the mean value of the diameter 9.18 nm. The effective anisotropy constant  $K_{eff}$  includes the magnetocrystalline anisotropy, the shape anisotropy, the surface anisotropy, and the dipolar interactions among MNPs.<sup>22</sup> Shape anisotropy is not relevant to the sphere case. Our  $K_{eff}$  for the 14.8 nm spheres is larger than the value ~42 kJ m<sup>-3</sup> for 14.9 nm monodisperse spherical magnetite nanoparticles in reference (*22*). This ~10 kJ m<sup>-3</sup> difference is likely due to dipolar coupling among our MNPs in the powder samples, assuming that magnetocrystalline anisotropy and surface anisotropy contributing to  $K_{eff}$  are the same for these two spherical MNPs with nearly the same size. At high temperature, surface anisotropy is insignificant in our MNPs with relatively large size (d > 5 nm).

### 5.4.4 FMR of the sphere, cube and poly MNPs

We recorded the FMR spectra of *dilute suspensions* of the sphere, cube and poly MNPs in octane, at a concentration of 0.01 wt% where the MNPs are non-interacting. In general, we find that the g value increases with an increase in MNP size. Lezama et al. also observed that the g value for a dilute suspension of MNPs increases with the particle size.<sup>13</sup> The change in the g value is related to the internal spin of the superparamagnetic MNPs and how the MNPs align with respect to the

external magnetic field. When MNPs are suspended in a fluid medium, the degree of alignment depends on Brownian and Neel's relaxation, as introduced in Chapter 1. We calculate the Brownian and Néel relaxation time for the three types of MNPs in **Table 5.1**. Based on the short time scale of Néel relaxation, the alignment is dominated by Néel mechanism. Recall in Chapter 1, the Neel's relaxation time is given by

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \tag{5.2}$$

Here the term KV is the internal anisotropy field of MNPs, where K is the anisotropy constant and V the volume. The term KV increases with particle size, so our MNPs with similar magnetic properties but with different size must have different resonance fields and g values. In short, the larger the size V, the larger the internal anisotropy field and therefore the larger the g value.



**Figure 5.6** FMR spectra of 0.01 wt% sphere, cube and poly MNPs in octane. The red dots indicate the resonance field and the corresponding g values. The black arrows indicate the sharp peak at g = 2.02 for sphere and poly MNPs. An orange downward arrow indicates the additional peak.

**Table 5.1** Characteristic Brownian and Néel relaxation times of the three types of MNPs. Detail

 calculation is found in supporting information 5.6.2.

	sphere	cube	poly
τ(Brownian)	$6.42 \times 10^{-7}  s$	3.78 ×10 <sup>-7</sup> s	$1.53 \times 10^{-7}  s$
τ(Néel)	9.81 ×10 <sup>-9</sup> s	$3.84 \times 10^{-9}  s$	1.72 ×10 <sup>-9</sup> s

The  $\Delta H_{pp}$  linewidths are 91 mT, 48 mT and 74 mT for the sphere, cube and poly MNPs, respectively. Because the observed linewidths correspond to non-interacting MNPs, they exhibit only magnetocrystalline anisotropy. Following the first order analysis of Weiss et al.,<sup>8</sup> the linewidth is given by

$$\Delta H_{pp} \sim \frac{5}{_3} H_a = \frac{5}{_3} \left(\frac{2K_1}{M_s}\right)$$
(5.3)

where  $H_a$  is the anisotropy field,  $K_1$  is first order magnetocrystalline anisotropy constant and  $M_s$  is the saturation magnetization. With  $M_s$  from SQUID magnetometry and the linewidth from FMR spectra, we calculate  $K_1$  to be 9.74 kJ/m<sup>3</sup> for sphere, 5.44 kJ/m<sup>3</sup> for cube, and 8.41 kJ/m<sup>3</sup> for poly samples. The  $K_1$  for bulk phase magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) are 13.5 kJ/m<sup>3</sup> and 4.65 kJ/m<sup>3</sup>, respectively.<sup>23</sup> It is well-established that the surfaces of magnetite nanoparticles are subject to oxidation, forming a maghemite outer layer.<sup>24</sup> Therefore, the lower value of  $K_1$  in our MNPs than bulk magnetite may be due to mixed magnetite (Fe<sub>3</sub>O<sub>4</sub>) and surface maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) in our MNPs.

We observe a narrow line at around 330 mT (g = 2.02) for the sphere and poly MNPs (**Figure 5.6**). This feature is consistent with the experiment reported earlier.<sup>11</sup> The origin of the sharp resonance has been the subject of debate.<sup>10</sup> The narrow line has been attributed to quantum transitions, based
on the "giant spin" model proposed by Noginova et al.<sup>10</sup> Others attribute the signal to a fraction of ultrafine MNPs (< 5 nm) which may show quantum effects.<sup>25</sup> Ultrafine MNPs were also present in the experimental work of Noginova et al.<sup>10</sup> We did observe some ultrafine particles for the sphere and poly MNPs by transmission electron microscopy (TEM), but not for the cube (**Figure 5.4**). The narrow signal feature is not observed in the cube sample. This result suggests that the narrow line may originate from adventitious ultrafine MNPs.

Note that in **Figure 5.6**, FMR from the dilute cube sample shows a band shoulder at 195 mT (g = 3.42) superimposed on the main low field band. This feature may originate in partial alignment along the [100] hard axis of the cube. The main band is dominated by the response due to MNP [111] easy axis orientation. We explain the shoulder at low field as follows. We refer to the time scale for MNP relaxation by the Brownian and Néel mechanisms in **Table 5.1** (the calculation in Section 5.6.2). The relaxation of a cube MNP is governed by the faster Néel mechanism, which is on the order of nanoseconds. This time scale is comparable to the time resolution of the FMR measurement.<sup>26</sup> It is therefore likely that the FMR signal can distinguish the two [100] and [111] orientations in colloidal suspensions of cube MNPs. Such easy and hard axes do not exist in the sphere and poly MNPs because they have a rotational symmetry on average. Therefore, no shoulder peak is observed in their FMR response.

### 5.4.5 Spike superstructure of MNPs

Having estimated the magnetocrystalline anisotropy for the non-interacting MNP system, we now turn to the interacting MNP systems—MNPs in spikes. Macroscopic conical spikes were obtained by evaporation mediated self-organization of MNPs in the presence of an inhomogeneous magnetic field (as described in Chapter 2). A spike is essentially a superstructure of MNPs; in other words, each MNP is an "artificial atom" and the spike is their macroscale "crystal". The conical spikes have an aspect ratio of height/diameter  $\sim 1.82 \text{ mm} / 0.47 \text{ mm} \approx 4$  unless otherwise specified (**Figure 5.7**). In contrast to a powder of randomly oriented MNPs, we expect the spike to exhibit magnetic anisotropy that result from MNP ordering, and spike orientation and shape. To ensure the reproducibility in the FMR experiment, we use spikes only from the center of the pattern in this work.



**Figure 5.7** Left panel shows an image of an array of trapped conical spikes array with hexagonal symmetry. Right panel shows an SEM image of a conical spike extracted from near the center of the array.

### 5.4.6 Reproducibility of FMR parameters for spikes

To develop a metric for reproducibility of the FMR spectra obtained from the spikes, we sampled four spikes extracted from the central area and from the same pattern derived from octane-based ferrofluids of sphere MNPs. We refer to these spikes as S-spikes. As shown in **Figure 5.8**, their FMR spectra in parallel (solid lines) and perpendicular orientations (dashed lines) are similar. The main difference arises in changes in the lineshape between 212 mT and 373. This region is demarcated by the vertical turquoise dotted lines that intersect close to crossing points for the spectra acquired from spikes in the two orthogonal orientations. The resonance fields  $H_{\rm res}$  for all four spikes are located near 212 mT (//) and 373 mT ( $\perp$ ), the difference being largely due the precision in reproducibly positioning the spikes. The resonance fields differ by no greater than 5 mT, so we adopt the  $H_{\rm res}$  difference as our criterion of reproducibility of sample position and properties. For simplicity, we refer to the resonance field for parallel and perpendicular orientations as  $H_{\rm res,\perp}$  and  $H_{\rm res,\perp}$ .



**Figure 5.8** FMR spectra of four S-spikes from a pattern derived from in octane. The two blue dotted lines indicate the resonance field positions for parallel and perpendicular orientations at 212 mT and 373 mT, respectively. The lineshape shows differences inside the boundaries of this region.

Unlike the resonance field, the linewidths for the four spikes differ: the linewidths from spikes oriented parallel to the field vary from 97 mT to 144 mT, while linewidths for the perpendicular orientation vary from 103 mT to 157 mT (**Table 5.2**). The linewidth for spike 2 does not depend on its orientation with respect to the field. This is also true of spike 3, this spike shows a broader linewidth than spike 2. The linewidth from spike 1 oriented perpendicular is larger than that in parallel by ~24 mT, and the linewidth from spike 4 differs by ~50 mT. The linewidth is affected by a number of factors that contribute to the distribution of magnetic anisotropy energy in the MNP systems. These factors include size, shape, composition, porosity and others.<sup>27</sup> The origin of the variation in linewidth among the four spikes is not known, but we surmise that the differences may be due to the fact that spikes are formed in a nonuniform magnetic field. Spikes tilt away from the central spike in conformity with the field gradient that creates the pattern and to minimize interspike repulsions (**Figure 5.7**).

 Table 5.2 Linewidth and resonance field of the four spikes in parallel and perpendicular orientations (unit: mT)

Spike sample	Spike 1	Spike 2	Spike 3	Spike 4
$H_{ m res}\left(/\!/,\perp ight)$	210, 374	213, 370	214, 374	212, 374
$\Delta H_{ m pp}\left(/\!/,\perp ight)$	97, 121	100, 103	144, 147	107, 157

#### 5.4.7 Angle dependence of spikes

Now we return to evaluate the FMR of spikes consisting of sphere, cube and poly MNPs. We shall refer them to as S-spike, C-spike and P-spike, respectively. To determine the magnetic anisotropy,

we record the angle dependent FMR spectra of a spike by rotating it with respect to the external magnetic field. The angular dependence of  $H_{\text{res}}$  for the three spikes is shown in **Figure 5.9A**. The spikes exhibit a well-defined uniaxial anisotropy, with the resonance field oscillating between minima along the vertical axis  $\theta = 0^{\circ}$  and  $180^{\circ}$ , and maxima along the base at  $\theta = 90^{\circ}$  and  $270^{\circ}$ . Among the three samples,  $H_{\text{res},//}$  of the S-spike is the lowest; while  $H_{\text{res},\perp}$  for all spikes are close to 370 mT. The shift in  $H_{\text{res}}$  from the reference field  $H_{\text{r}} = 332$  mT is due to the anisotropy field  $H_{\text{a}}$  of the spike.<sup>12</sup> The anisotropy fields  $H_{\text{a}}$  can be estimated by the separation of  $H_{\text{res},\perp}$  and  $H_{\text{res},//}$ , which are 172 mT, 148 mT, 124 mT for S-spike, C-spike and P-spike samples, respectively.



**Figure 5.9** Angle dependence of FMR parameters for S-spike, C-spike and P-spike. (A) Plot of  $H_{\text{res}}$  versus angle (B) Plot of  $\Delta H_{\text{pp}}$  versus angle.

When an S-spike is ground to powder, the separation of  $H_{\text{res},\perp}$  and  $H_{\text{res},\parallel}$  decreases drastically to 25 mT (see supporting **Figure S5.4**). The difference of the demagnetization field for this spike is given by  $\mu_0(N_z-N_x)M_s$ , where  $N_z$  and  $N_x$  are the demagnetization factors along the *z*- and *x*-axis of the spike. Assuming that the shape of the spike is the same for all samples, the term  $(N_z-N_x)$  is fixed and the difference of the demagnetization field scales with  $M_s$ . From SQUID magnetometry,

we know that  $M_s$  is largest for poly MNPs and yet P-spike has the smallest  $H_a$  among the spikes. This suggests that other sources of anisotropy may contribute to the anisotropy field  $H_a$ .

Figure 5.9B shows that the linewidths  $\Delta H_{pp}$  of the S-spike and C-spike are greater than those of their dilute fluid suspension counterparts. This indicates that in addition to the magnetocrystalline anisotropy, other kinds of anisotropy contributing to the linewidth broadening, in addition to the magnetocrystalline anisotropy. The linewidth of the S-spike matches with that of the C-spike in the parallel position ( $\theta = 0^{\circ}$ ), but at other angles the S-spike has a lager  $\Delta H_{pp}$  than the C-spike (Figure 5.9B). Note that  $\Delta H_{pp}$  of 75 mT determined for the P-spike is identical within experimental error to  $\Delta H_{pp}$  for its dilute poly MNP suspension in octane. This  $\Delta H_{pp}$  for P-spike may originate only from its own magnetocrystalline anisotropy (which yields a linewidth of 74 mT). We have no further explanation for this at this stage. Nevertheless, for the S-spike and C-spike, it makes sense that the larger linewidths must depend on complex 3D dipolar interactions (with some degree of orientational particle ordering at the mesoscale).

We argue that FMR of spikes is due to the collective response of the ensemble of the constituting MNPs. Our position is supported by the work by Trunoava et al. <sup>28</sup> They simulated the FMR signals of nanocubes oriented at different angles to the external field. The sum of these signals is similar to the lineshape observed in our spike samples (**Figure 5.10**). This suggests that most of easy axes of the MNPs are aligned with the external field for the spike parallel to the external field, whereas most hard axes of the MNPs are aligned with the field in perpendicular orientation. In turn, the lineshape reflects the trapped orientations of the nanoparticles in the spike structures.



**Figure 5.10** Comparison of (A) simulated FMR spectra of an ensemble of nanocubes from Trunoava et al. (28) In (a) simulation of FMR lines for nanocubes oriented from easy to hard direction with respect to the  $B_0$  field. The black curve is the sum of all colored resonance lines. In (b) theoretical fits (red lines) to the in plane and out of plane experimental FMR spectra for nanocubes (light colored dots). Reprint from reference (28) with permission from AIP Publishing (2008). (B) our experimental FMR spectra for spikes. Solid lines refer to parallel (in-plane) orientation of spikes. Dashed lines refer to perpendicular (out-of-plane) orientation of spikes.

#### 5.4.8 Low temperature FMR spectra of spikes

FMR spectra were obtained for spikes oriented parallel and perpendicular to the external magnetic field over the temperature range 120 to 290 K (**Figure 5.12A–F**). The general features observed in these systems are as follows: with decreasing temperature,  $H_{res}$  shifts to lower fields and  $\Delta H_{pp}$ increases (**Figure 5.11**). For parallel field alignment, all three spike samples exhibit a decrease in  $H_{res}$  and broadening of  $\Delta H_{pp}$  with decreasing temperature. These occur in the order:

$$H_{\rm res}({\rm S-spike}) < H_{\rm res}({\rm C-spike}) < H_{\rm res}({\rm P-spike});$$

$$\Delta H_{pp}$$
 (S-spike) >  $\Delta H_{pp}$  (C-spike) >  $\Delta H_{pp}$  (P-spike).

For perpendicular alignment, we observe several temperature regimes:

Above 260 K,  $H_{res}$  (S-spike) >  $H_{res}$  (C-spike) >  $H_{res}$  (P-spike); In 240–260 K,  $H_{res}$  (P-spike) <  $H_{res}$  (S-spike) <  $H_{res}$  (C-spike); In 200–220 K,  $H_{res}$  (S-spike)  $\approx H_{res}$  (C-spike)  $\approx H_{res}$  (P-spike);

Below 200 K,  $H_{res}$  (S-spike)  $\leq H_{res}$  (C-spike)  $\leq H_{res}$  (P-spike).



**Figure 5.11** (A) Plot of the resonance field  $H_{res}$  of the three spikes versus temperature (B) Plot of the linewidth  $\Delta H_{pp}$  of the three spikes versus temperature.

The shift of  $H_{\text{res}}$  to lower field and the increase in  $\Delta H_{\text{pp}}$  is typical for *non-interacting* superparamagnetic nanoparticle systems.<sup>29-32</sup> We also observe the similar change in FMR parameters for our spikes which comprise *interacting* superparamagnetic nanoparticles. This means that the  $H_{\text{res}}$  shift and the  $\Delta H_{\text{pp}}$  broadening are due to the intrinsic properties of MNPs—the superparamagnetic and surface effects of MNPs. Let us elaborate. Raikher and Stepanov (RS) introduced a model for FMR in superparamagnetic nanoparticle systems that includes thermal reorientation of magnetic moments.<sup>12, 33</sup> At low temperature or in ambient temperature solids, the magnetization of MNPs relaxes by Néel's mechanism where this relaxation time is given by

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \tag{5.4}$$

Here  $\tau_0$  is the characteristic time ~10<sup>-10</sup> s, *K* is the anisotropy constant, *V* is the particle volume,  $k_B$  is Boltzmann constant and *T* is temperature. When the temperature is lowered, the relaxation time—the time it takes for MNPs to align to the field—increases. As a result, the spectrometer detects more unaligned spins in the experimental timeframe of 10<sup>-9</sup> s. The random distribution of magnetic moments in the spikes results in inhomogeneous broadening, according to the RS model. A contribution to the shift/peak broadening can originate in surface effects at low temperature. These are described as the change in exchange anisotropy arising at the ferromagnetic cores and antiferromagnetic layers within MNPs. This change may shift the FMR lines to low fields.<sup>34, 35</sup>



**Figure 5.12** FMR spectra of (A) S-spike in parallel and (B) in perpendicular orientation, (C) C-spike in parallel and (D) in perpendicular orientation, and (E) P-spike in parallel and (F) in perpendicular orientation. (G) Simulated FMR spectra for mixtures of magnetotactic bacteria (isolated magnetite chains) with non-chain magnetite. In the four examples, black lines correspond to 100% magnetosome chains and light green lines to 0% chains. Reprint from reference (8) with permission (2004) Elsevier.

We note an interesting feature in the spectra for the perpendicular orientation: the high field peaks remain mostly in position with what appears to be an isosbestic point at around 390 mT for S-spike, 385 mT for C-spike, and 370 mT for P-spike. (Figure 5.12B, D and F) This high-field component changes intensity only with temperature, suggesting that it may come from some temperature-independent property of the spike sample, e.g. an organization of MNPs. Its

temperature dependent intensity variation is reminiscent of the FMR spectra obtained and simulated by Weiss et al. on single domain magnetite nanoparticles from magnetotactic bacteria.<sup>8</sup> They showed a series of FMR spectra for pure chains of MNPs mixed with randomly oriented polycrystalline magnetite (**Figure 5.12G**). The high-field peak located at around 400 mT increases its intensity when the mass fraction of chains increases. We understand that the intensity decrease for the high-field peak in our spikes is due to a decrease in temperature. This is in line with the RS model described earlier, where more magnetic moments may be randomized at lower temperature. Based on the similarity in FMR spectra shown in **Figure 5.12**, the high field peak may arise from chain-like organization of MNPs in the spikes. We then turn to high resolution SEM of the spikes to see if chains of MNPs exist.

**Figure 5.13** shows the SEM of the S-spike and the C-spike. Sphere MNPs are organized into a defected rhombic lattice (**Figure 5.13A–B**), where long-range order can be observed in three directions as shown. Some vacancies are present in the rhombic lattice. Cube MNPs, on the other hand, are organized into short chains which pack together at the surface with no obvious long-range order (**Figure 5.13C–D**). The short chains orient predominantly in the cross-section plane of the spike. These observations indeed support the argument that the isosbestic features in FMR lines may be due to chains. This kind of structuring is higher in energy than close packed superlattices of hcp and bcc, indicating the spike superstructure is non-equilibrium kinetically trapped. To the best of our knowledge, this is the first observation of nanoscale ordering of the spike structures in ferrofluids.



**Figure 5.13** High resolution SEM of the spike surface for S-spike and C-spike. The spike sample is oriented horizontally. (A) area near the tip of the S-spike (B) area near the base of the S-spike. Blue circles guide eyes for short-range order. (C) area near the tip of the C-spike (D) area near the base of the C-spike. Orange rectangles show some short chains of nanocubes. The scale bar is 100 nm.

As mentioned before in Section 5.4.6, the linewidth varies from spike to spike. It is therefore meaningless to compare the linewidth between the three MNP types. Here we analyze the linewidth for each spike separately with a phenomenological model introduced by Nagata and Ishihara to predict orientation of MNPs.<sup>36</sup> They write the change in  $H_{res}$  with temperature as  $\delta H_{res} =$  $H_{ref} - H_{res}(T)$ , where  $H_{ref}$  is taken as the resonance field of non-interacting MNPs. Their model predicts that  $\delta H_{res} \simeq (\Delta H_{pp})^n$ , where n = 2 for partially oriented MNPs and n = 3 for randomly oriented MNPs. This model has been validated for many systems.<sup>30, 32, 37-39</sup> We fit our data to Nagata and Ishihara's model. The log-log plots of  $\delta H_{res}$  and  $\Delta H_{pp}$  of the fitting are shown in Section 5.6.5. The slopes of the fitted lines for all the parallel positioned spikes are below 2. This indicates MNPs in the spikes are strongly oriented along the parallel direction. The spikes in the perpendicular orientation cannot be fitted with this model. To summarize the low temperature study, all the spikes exhibit some ordering both in parallel and perpendicular orientations, regardless of the MNP type.

#### 5.4.9 FMR of oleic acid-doped spikes

Now we investigate if a change in dipolar interactions among MNPs can cause the FMR lines to shift by increasing the interparticle distance in the spike superstructure. Note that each MNP is coated with a layer of oleic acid with a chain length of ~2 nm. In spikes, the spacing between MNPs is presumably ~2 nm, at which exchange interaction is negligible.<sup>40</sup> Dipolar interactions therefore mainly contribute to the anisotropy field  $H_a$  that shift  $H_{res}$ . To increase the distance between MNPs, an excess of oleic acid (OA) ligand was added to the ferrofluids prior to solvent evaporation (similar to the formulation used in Chapter 3). By TGA in Chapter 3, the resulting spikes thus contain more oleic acid within the superstructures. The FMR spectra of the resulting spikes for all MNPs are collected in **Figure 5.14A**, **B** and **C**. The lineshape for spikes of each MNP is similar but  $H_{res,ll}$  shifts to higher field and  $H_{res,ll}$  shifts to lower field with increasing OA. The anisotropy field  $H_a$  therefore decreases (**Figure 5.14D**).

Both intrinsic anisotropy of MNPs or interparticle interactions can contribute to a change in the anisotropy field  $H_a$ .<sup>41</sup> For each spike of the same type of MNPs, the intrinsic anisotropy of MNPs

is the same. Therefore, the change in  $H_a$  depends on interparticle interactions. The impact of adding oleic acid is that the average distance between the MNPs increases within the spike superstructure, similar to a process of dilution. The dipolar interaction field can be estimated from  $H_{dd} \sim m^2/d^3$ , where *m* is magnetic moment and *d* is the mean distance between the particles.<sup>42</sup> The interparticle dipole-dipole interactions that scale inversely with  $d^3$  therefore quickly fall off. Its contribution to the magnetic anisotropy  $H_a$  decreases. The complicated lineshape in these FMR spectra requires further experiments to explain the change in  $\Delta H_{pp}$ .



**Figure 5.14** Outcome of adding excess oleic acid (OA) to the spike superstructure. (A) S-spike (B) C-spike (C) P-spike (D) Plot of  $H_{res}$  versus the amount of excess OA (E) Plot of  $\Delta H_{pp}$  versus the amount of excess OA. Solid lines denote the parallel orientation and dotted lines the perpendicular orientation.

### 5.4.10 Magnetic anisotropy of the spike superstructure

To summarize, magnetic anisotropy of self-organized MNP superstructures differs from the individual MNP and from the bulk counterparts. Individual non-interacting MNPs are dominated by intrinsic magnetocrystalline anisotropy, surface anisotropy and particle shape anisotropy. Bulk phase materials are dominated by intrinsic magnetocrystalline anisotropy and bulk sample shape anisotropy. All these anisotropy terms may contribute to the total magnetic anisotropy of self-organized MNP superstructures.

Our spikes are attracted to nonmagnetic metal tweezers (**Figure 5.15**). The magnetic field strength of a spike was determined to be ~0.12 mT by a Gaussmeter. This is clearly superferromagnetic (SFM) behavior, where ferromagnetism arises from interacting superparamagnetic nanoparticles.<sup>1</sup> **Figure S5.8** shows the FC/ZFC curves for the S-spike compared with sphere MNPs in powder form. The blocking temperature for the S-spike is found to be 254 K, identical to that of sphere MNP powder. Clearly, more SQUID magnetometry study is required to understand the SFM properties of the spikes.



Figure 5.15 Five spikes attract to the two arms of a metal tweezer.

## 5.5 Conclusion

In conclusion, we investigated the FMR response of sphere, cube and polydisperse MNPs in noninteracting and interacting configurations. For non-interacting MNPs, the resonance field depends on the particle size. From the FMR linewidth for non-interacting MNPs in dilute suspensions, we determine  $K_1$  to be 9.74 kJ/m<sup>3</sup> for sphere, 5.44 kJ/m<sup>3</sup> for cube, and 8.41 kJ/m<sup>3</sup> for poly MNPs. This  $K_1$  is the intrinsic magnetic anisotropy of the MNPs. For interacting MNP systems, we focus on the FMR for spike superstructures. The non-equilibrium spike structures exhibit superferromagnetic behavior. Both angle dependence and low temperature study confirm the magnetic anisotropy for the spikes. The resonance field shifts, and the linewidth broadens for interacting MNPs. Dipolar interaction in the spike superstructures can be fine-tuned by controlling the interparticle distance. More study is required to uncover the contributions to the complicated FMR lineshape and linewidth.

# 5.6 Supporting Information



## 5.6.1 Size distribution of MNPs with lognormal fit

Figure S5.1 Size distribution of sphere MNPs with a lognormal fit.



Figure S5.2 Size distribution of cube MNPs with a lognormal fit.



Figure S5.3 Size distribution of polydisperse MNPs with a lognormal fit.

## 5.6.2 Calculations

The Brownian and Néel relaxation time in ferrofluid suspensions for different MNPs are calculated as follows.

Sphere:

$$\tau_B = \frac{3V_h \eta_0}{k_B T} = \frac{3 \times [\pi/6 \times (14.8 \times 10^{-9})^3] \times 0.00051}{1.38 \times 10^{-23} \times 293} = 6.42 \times 10^{-7} \text{s}$$
$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) = 10^{-9} \exp\left(\frac{5.44 \times 10^3 \times [\pi/6 \times (14.8 \times 10^{-9})^3]}{1.38 \times 10^{-23} \times 293}\right) = 9.81 \times 10^{-9} \text{s}$$

Cube:

$$\tau_B = \frac{3V_h \eta_0}{k_B T} = \frac{3 \times [(10.0 \times 10^{-9})^3] \times 0.00051}{1.38 \times 10^{-23} \times 293} = 3.78 \times 10^{-7} \text{s}$$
$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) = 10^{-9} \exp\left(\frac{5.44 \times 10^3 \times [(10.0 \times 10^{-9})^3]}{1.38 \times 10^{-23} \times 293}\right) = 3.84 \times 10^{-9} \text{s}$$

Poly:

$$\tau_B = \frac{3V_h \eta_0}{k_B T} = \frac{3 \times [\pi/6 \times (9.18 \times 10^{-9})^3] \times 0.00051}{1.38 \times 10^{-23} \times 293} = 1.53 \times 10^{-7} \text{s}$$
$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) = 10^{-9} \exp\left(\frac{5.44 \times 10^3 \times [\pi/6 \times (9.18 \times 10^{-9})^3]}{1.38 \times 10^{-23} \times 293}\right) = 1.72 \times 10^{-9} \text{s}$$

#### 5.6.3 FMR spectra of fractured spike

This section reports on our study of the effect of conical shape on the FMR response of the spike structures. We orient a spike comprising of spherical MNPs parallel and perpendicular to the electromagnet in the spectrometer. The resonance field of the parallel position increases from 199 mT to 370 mT for the perpendicular orientation, along with an increase of linewidth ( $\Delta H_{PP}$ ) from 123 mT to 156 mT (**Table S5.1**). To reveal the effect of ordering of MNPs at finer scales, the spike was broken into small pieces. The macroscopic shape anisotropy due to the cone geometry is lost, but the alignment of MNPs at the nanoscale persists. **Figure S5.4** shows the corresponding FMR spectra that were acquired in the parallel and perpendicular orientations, respectively. The diminished contribution of macroscopic ordering is reflected in the decrease in the  $H_{res}$  difference from 171 mT to 26 mT. The linewidths of both orientations increase significantly by around 50 mT. The linewidth decreases when comparing the powder to a conical spike is reminiscent of the dipolar narrowing effect seen in polycrystalline samples.<sup>43</sup>



Figure S5.4 FMR spectra an S-spike and its grounded form.

**Table S5.1** Linewidth and the resonance field of a spike and its ground form in parallel and perpendicular orientations (unit: mT)

	Fractured //	Fractured ⊥	Spike //	Spike ⊥
$\Delta H_{ m pp}$	178	203	123	156
Hres	232	258	199	371

# 5.6.4 Summary of the FMR parameters for our samples

Sample	g value	$\Delta H_{\rm pp}~({\rm mT})$			
MNPs in octane					
sphere	2.35	91			
cube	2.33	48			
poly MNPs	2.23	74			
MNP spikes					
S-spike (//, ⊥)	3.35, 1.80	123, 156			
+ 1.3% OA	2.98, 1.82	141, 152			
+ 3.0% OA	2.87, 1.86	163, 124			
C-spike (//, ⊥)	2.99, 1.80	126, 138			
+ 1.3% OA	2.79, 1.83	167, 174			
+ 3.0% OA	2.54, 1.88	145, 144			
P-spike (//, ⊥)	2.76, 1.82	75, 74			
+ 1.3% OA	2.62, 1.79	126, 143			
+ 3.0% OA	2.46, 1.85	80, 103			

**Table S5.2** Summary of the g values and linewidth of the FMR spectra.

OA	0%	1.3%	3.0%
S-spikes			
$\Delta H_{ m pp}$	123/156	141/152	163/124
H <sub>res</sub>	199/371	224/367	232/358
C-spikes			
$\Delta H_{ m pp}$	126 /138	167/174	145/144
H <sub>res</sub>	223/370	239/365	263/356
P-spikes			
$\Delta H_{ m pp}$	75/74	126/143	80/103
H <sub>res</sub>	242/366	255/372	271/361

 Table S5.3 Normalized FMR spectra of OA added spikes. (unit: mT)



5.6.5 Fitting results of our data to the Nagata and Ishihara's model

**Figure S5.5** Fitted log-log plots of  $\delta H_{\text{res}}$  and  $\Delta H_{\text{pp}}$  for the S-spike in parallel orientation.



**Figure S5.6** Fitted log-log plots of  $\delta H_{res}$  and  $\Delta H_{pp}$  for the C-spike in parallel orientation.



**Figure S5.7** Fitted log-log plots of  $\delta H_{res}$  and  $\Delta H_{pp}$  for the P-spike in parallel orientation.

## 5.6.6 Additional data



**Figure S5.8** ZFC/FC curves of the spherical MNPs and a sphere-based spike. The blocking temperature of the spike is determined to be 254 K.

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# **Chapter 6 Conclusions and Outlook**

### 6.1 Conclusions

This thesis has been concerned with the nanoscale to macroscale origins of pattern formation and aspects of self-organization in ferrofluid systems whose patterns can be kinetically trapped. Ferrofluids are paradigms for pattern formation, a phenomenon that is ubiquitous in nature and contrived matter. Although the macro-patterns of conical spike structures in conventional ferrofluids have long been studied, little is known about the ultrastructure of the arrangements of magnetic nanoparticles from which they are made. Even less is known about the impact of control variables like ligand, host solvent type, host reaction-diffusion events and other chemical and physical parameters on pattern evolution, pattern phase stability and pattern interconversion.

To address some of the effects of these parameters, we reformulated ferrofluids from volatile alkane solvents so that their patterns could be "trapped" as kinetically stable structures. The trapped structures are assembled from oleic acid-coated magnetite nanoparticles. Oleic acid participates in the kinetic trapping process, most likely via ligand-solvent interactions to ligandligand interdigitation during magnetic field alignment. In this context, we examined the impact on patterning of an inhomogeneous magnetic field, nanoparticle concentration, evaporation rate, solvent type and substrate. Solvent evaporation results in kinetic trapping of the self-organizing structures, introducing irreversibility in ferrofluid patterning. We showed how pattern entropy, spike number and pattern wavelength depend on control parameters like nanoparticle magnetization, magnetic field strength and gradient, nanoparticle concentration, evaporation rate, solvent type and substrate interface. Vibrational spectroscopy suggests how oleic acid and its ordering on the magnetic nanoparticle surface may be implicated in the structural stability of the self-organized structures in the absence of covalent bond formation. We showed that excess oleic acid ligand, in concert with a complex ferrohydrodynamic response, directs changes in the macroscopic patterns from order to disorder, and transitions from hexagonal to labyrinthine patterns. A crosslinking polymer was introduced as an example of a reaction-diffusion system where the exchange of matter in an applied magnetic field induces a new type of morphogenesis. We observed previously unreported hierarchies of order spanning nanometers to millimeters in these trapped reaction-diffusion systems. We established that microscale spike morphology is influenced by controlled changes in the ambient humidity of the reaction environment. Electron microscopy of thermally induced solid-state transformation of spike structures revealed how magnetic nanoparticles may be ordered at the mesoscale. The spikes were shown to be constructed of ordered nanoparticle layers. Magnetic nanoparticles are ordered in a rhombic lattice in the spike superstructures. Magnetometry and ferromagnetic resonance provide new insight into magnetic field induced order and interacting magnetic nanoparticles in the spike structures.

### 6.2 Future Directions

This thesis lays groundwork for manipulating magnetic nanoparticles in a variety of host media. Here we outline some directions for future work based on findings described in the thesis.

#### 6.2.1 Relation between number of spikes and saturation magnetization

In Chapter 2, we present a preliminary correlation between the number of spikes N in the Rosensweig pattern and the saturation magnetization  $M_s$  of the magnetic nanoparticles. The strength of this correlation needs further testing in relation to magnetic nanoparticles of different saturation magnetization and other applied magnetic fields. It is recommended that some effort be made to derive an empirical relation among the variables by carrying out more experiments with magnetic nanoparticles in different magnetization regimes. If confirmed, such correlation may be a useful metric to provide rough estimates of saturation magnetization of magnetic nanoparticles without resorting to more costly magnetometry.

#### 6.2.2 Choice of nanoparticles

Iron oxide nanoparticles were used throughout this thesis. We suggest expanding the repertoire of nanoparticles to:

(1) FePt, Co, FeC, MnO<sub>3</sub>, and other metal-doped ferrites. Each type of nanoparticle possesses unique magnetic properties and the binary and multinary combination of different MNPs in the self-organized superstructure may show different collective responses;

(2) co-combinations of magnetic nanoparticles with nonmagnetic nanoparticles, such as Au, Ag, CdSe and other quantum dots. Other nonmagnetic nanoparticles that exhibit plasmonic or tunable
optical properties may be incorporated into self-organized superstructures, yielding a combination of magnetic and plasmonic or optical properties.

# 6.2.3 Control parameter—magnetic fields

Changing the applied magnetic field by motion control of the magnet is recommended to add another level of complexity to the dynamic assembly of MNPs. We have preliminary results on pattern formation in evaporative ferrofluids under a rotating magnetic field. A rotation platform was used to rotate the magnet while keeping the sample in place. During evaporation, we observed that the whole hexagonal array is under circular motion until the solvent evaporates completely. The trapped pattern shown in **Figure 6.1A** has 66 spikes and its counterpart in a static field shown in **Figure 6.1B** has 60 spikes. The nanoscale ordering of monodisperse MNPs in the fixed spike superstructures in the rotating magnetic field may be different from that in a static field. The collective magnetic properties may also be different. We also recommend studying the effects of AC magnetic fields, homogeneous magnetic fields and 3D magnetic fields on pattern formation in kinetically trapped ferrofluids.



**Figure 6.1** Trapped pattern derived from 165 mg ferrofluids of 20 wt% MNPs in octane in the presence of (A) a rotating magnetic field of 140 mT and (B) a static magnetic field of 140 mT.

# 6.2.4 Control parameter—solvent effects

There is wide scope to advance the studies on kinetic trapping in relation to the host solvent type. We recommend continuing research into the impact of solvent type and solvent combination as control parameters of pattern formation and ultrastructure. In this thesis, we have used alkane solvents to host magnetic nanoparticles in ferrofluids. In our experience, other aromatic and halogen solvents, e.g., toluene, cyclohexane, chloroform tend to yield defective patterns. Yet Quan et al. have shown that colloidal Pt nanocubes will self-organize into two types of distinct superstructures that depend on solvent type, aliphatic hexane versus aromatic toluene.<sup>1</sup> In Chapter 2, we observed that octane-based ferrofluid yields the lowest number of spikes among C6–C10 alkane. But why octane (C8)? We postulated that alkane solvents with different chain length may interact with oleic acid differently, and that this interaction might be linked to the patterns that are produced. We recommend detailed study of this conjecture.

#### 6.2.5 Control parameter—substrate

In Chapter 2 we showed that ferrofluid patterning is influenced by the polystyrene, glass, Teflon and silicon substrates, but the underlying details of the forces at play and their significance need testing and development. To extend the study, ferrofluid patterning can also be carried out on superhydrophobic substrates,<sup>2</sup> and superomniphobic surfaces.<sup>3</sup> The interaction between ferrofluids and these surfaces is reduced. In this case, the impact of surface energy should be minimized, and one may examine the effect of magnetic susceptibility on pattern formation.

In addition, the substrates can also be customized to have pre-patterns and different dimensions, depending on the applications. Yin et al. have demonstrated self-assembly of magnetic particles

into 2D photonic labyrinth structures in a patterned substrate.<sup>4</sup> Methods to customize the substrates might include 3D printing and machining. In 3D printing, the object is typically constructed layer by layer. One major challenge to consider is that surface smoothness is limited by the nozzle. In machining, the material parts are drilled by a machine aided by Computer Aided Design (CAD) and Computer Aided Manufacturing (CAM) programs. This fabrication process can be used to produce patterned substrate with millimeter precision. In short, much more can be done to customize the substrate for MNP self-organization and to explore the effect of different kinds of substrates.

### 6.2.6 Control parameter—film thickness

Other than forming spike pattern, ferrofluids show magnetic field induced birefringence. This is a thin film phenomenon that arises from variations in refractive index caused by anisotropic alignment of MNPs in the fluid medium. We recommend experiments to explore this phenomenon in the context of 1D and 2D photonic stopband structure, including chirped and graded index grating structures in these dimensions. It is therefore interesting the make a permanent 1D structure from monodisperse MNPs and then record a second permanent magnetic field induced grating on top, rotating the sample through various angles to systematically vary the lattice type from diamond, to rhombic, or to square.



**Figure 6.2** Colors observed from a months-old sample of the pattern derived from a polymerbased ferrofluid. The color changes near the base of the spikes in the pattern, from yellow to purple to blue to green, and then back to yellow and purple. The color does not change with viewing angles.

Chapter 4 describes a polymer-based ferrofluid system that generates unique ordered structures at mesoscale. Surprisingly, some of our early samples of the polymer-based pattern developed color after sitting for several months. This is evident in **Figure 6.2** where the color travel phenomenon may result not from simple thin film interference, but of visible domain diffraction from an ordered lattice of MNPs. It is clear that the color develops in the thin film structures near the base of the spikes. Therefore, we recommend studies of patterning in kinetically trapping media as functions of film thickness. Decreasing film thickness will create new competition among growing spikes for material to feed the evolving pattern. In turn, this should impose new boundary conditions on patterning and phase stability, perhaps also on suppressing the spike pattern formation. The

"photonic crystal" fabrication method we suggest is far simpler than the multi-step method implemented by Yin and co-workers (cf. Chapter 4—the fiber "sheet" assemblies).<sup>4</sup>

#### 6.2.7 Control parameter—polymer

In Chapter 4, we demonstrated that the reaction-diffusion polymer based ferrofluid exhibit timevarying and humidity-sensitive complexity. We recommend further investigations to control the formation of the ordered state, especially those that resemble the "breath figure" patterns. In this context, controlling the formation of fiber-like arrays may be of interest to create magnetic functional surfaces. Additional work is needed to formulate the ferrofluids with respect to the relative humidity of environment. This may require lowering the concentration of MNPs and changing polymer type in the ferrofluid formulations.

### 6.2.8 Thermal transformation

In Chapter 4, we presented some exciting results on thermal transformation of the trapped structures of MNPs. It is interesting how ordering of MNPs can be transferred to their solid-state transformation products. With the binary or multinary combinations of nanoparticles in superstructures as suggested above in Section 6.2.2, thermal transformation reaction may yield many more materials with hierarchical structures that may have new properties. Care in this case should be given to the reaction conditions such as atmosphere, heating temperature, heating rate, holding time, heating steps, cooling rate, etc. To study this, a coupled TGA-FTIR-GCMS instrument might be useful to provide in situ information about the thermal transformation.

# 6.2.9 Ferromagnetic resonance

The investigation of the FMR response of spike superstructures of MNPs in Chapter 5 provides a solid basis from which further exploration of the lineshape and linewidth in the interacting MNP systems. In addition to the spike structures used in this thesis, other kinds of MNP superstructures may be used for FMR study. As mentioned in Chapter 5, it is not trivial to have a reproducible interacting MNP system. Systematic comparison among monodisperse MNPs of different sizes and shapes in interacting MNP system may open up opportunities to explore the collective magnetic response of the MNP systems and the contribution of dipole-dipole interactions to magnetic anisotropy.

# 6.3 Closing Remarks

Patterns are not just aesthetic-many are linked to functional structures. Nature provides countless examples of pattern formation over many length scales. After millions of years of selection and evolution, some of these patterns inspire biomimetic technology and materials science. Figure 6.3 shows some examples of naturally occurring functional patterns. The colorful iridescence of butterfly wings originates from electromagnetic field interaction with the nanostructured photonic crystals that have been identified in wing scales.<sup>5</sup> The excellent water repellency of lotus leaves can be traced to the nanoscale hierarchical roughness of their surfaces that can dewet liquids.<sup>6</sup> Abalone shell nacre consists of 95% layered aragonite (CaCO<sub>3</sub>) platelets connected by organic interlayers. It shows toughness much higher than that of calcium carbonate alone.<sup>7</sup> The high contrast stripes on zebra are believed to disorient biting flies that carry lethal diseases.<sup>8</sup> In biology, animal aggregation that occurs in numerous species may be beneficial to survivorship, mating, reproductive success, food finding, etc.<sup>9</sup> The chemical compositions of such complex biological patterns contain carbon, oxygen, hydrogen and nitrogen, which accounts for some 90 wt%. But knowledge of the underlying processes of how these basic elements evolve into a complex biological system (and us!) remains elusive-knowing the letters or words does not mean that we understand the poetry. Continued pursuit of the unifying features and the origins of self-organizing physical systems-their ontogenesis-may bring us closer to an answer.



**Figure 6.3** Examples of patterns in nature that are linked to functionality. (A) Optical micrograph of a butterfly wing (Scale bar: 100  $\mu$ m.) (B) SEM image of a wing scale showing a pattern of crystallites. (Scale bar: 2.5  $\mu$ m.) (C) Lotus leaves showing water repellency (D) SEM image of the hierarchical structure on the upper side of the lotus leaf. (E) Five levels of structures from nano to macro length scales in nacre. (F) Phylogenetic tree of zebras. Drawings by Rickesh Patel. (G) A school of fish (Photo: Brian J. Skerry/National Geographic Society/Corbis). (A) and (B) are reprinted with permission from reference (*5*), copyright 2010 National Academy of Sciences. (C) and (D) are reprinted with permission from reference (*7*), copyright 2008 American Association for the Advancement of Science. (F) is reprinted with permission from reference (*8*), copyright 2014 Nature Publishing Group.

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