Magnetization Dynamics and Interparticle Interactions in Ferrofluids and Nanostructures

Marienette B. Morales

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Magnetization Dynamics and Interparticle Interactions in Ferrofluids and Nanostructures

by

Marienette B. Morales

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Physics College of Arts and Sciences University of South Florida

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Keywords: magnetic colloids, nanoparticles, transverse susceptibility, relaxation phenomena, superparamagnetism

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DEDICATION

To my parents, for getting me started

To Ian and Baby Janna, for giving me the inspiration to finish
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LIST OF ABBREVIATIONS

AC
Alternating Current
CoFe$_2$O$_4$
Cobalt ferrite
DC
Direct Current
emu
Magnetic Moment Unit (Electromagnetic Unit)
Fe$_3$O$_4$
Magnetite/ Iron oxide
H
Magnetic Field
$H_K$
Anisotropy Field
$H_C$
Coercive Field (Coercivity)
J
Joule
K
Kelvin
M
DC-Magnetization
$M_R$
Remanent Magnetization
$M_S$
Saturation Magnetization
M-H
Magnetization vs. Applied Magnetic Field
MZFO
Manganese zinc ferrite
NA
Néel-Arrhenius
Oe
Oersted
PPMS
Physical Properties Measurement System
RF
Radio-Frequency
s
second
T
Tesla
$T_B$
Blocking temperature
\begin{tabular}{ll}
\emph{T}_F & Freezing temperature \\
TEM & Transmission Electron Microscope \\
TS & Transverse Susceptibility \\
VF & Vogel-Fulcher \\
XRD & X-Ray Diffraction \\
\end{tabular}
MAGNETIZATION DYNAMICS AND INTERPARTICLE INTERACTIONS IN FERROFLUIDS AND NANOSTRUCTURES

Marienette B. Morales

ABSTRACT

Nanoparticle assemblies are of current interest as they are used in a wide variety of industrial and biomedical applications. This work presents two studies aimed at understanding the magnetization dynamics and interparticle interactions in nanoparticle assemblies and various types of ferrofluids.

First, we studied the influence of varying strengths of dipolar interaction on the static and dynamic magnetic properties of surfactant-coated monodispersed manganese-zinc ferrite nanoparticles using reversible transverse susceptibility. We tracked the evolution of the anisotropy peaks with varying magnetic field, temperature, and interaction strength. The anisotropy peaks of weakly interacting particles appear as non-symmetric peaks and at lower fields in a unipolar transverse susceptibility scan. On the other hand, a strongly interacting particle system exhibits symmetric anisotropy peaks situated at higher field values.

In the second study, we successfully synthesized stable ferrofluids out of high quality Fe$_3$O$_4$ and CoFe$_2$O$_4$ nanoparticles. Such ferrofluids are excellent systems for the investigation of physics of relaxation phenomena in magnetic nanoparticles. Motivated by the need to understand their peculiar magnetic response, a comparative study on Fe$_3$O$_4$- and CoFe$_2$O$_4$-based ferrofluids was performed. We investigated cases in which particle blocking and carrier fluid freezing temperatures were close and far apart from each other. Our experimental results reveal the true origin of the glass-like relaxation peaks that have been
widely observed in ferrofluids by many groups but remained largely unexplained. Contrary to the speculation of previous literature, we argue that the formation of the magnetic anomaly is due not only to the particle blocking but also to its correlation with the carrier fluid freezing effects. It is also shown that the nature of these peaks is strongly affected by varying particle size and carrier fluid medium. Quantitative fits of the frequency dependent AC susceptibility to the Vogel-Fulcher scaling law clearly indicate that the blocking of magnetic nanoparticles in the frozen state significantly affects the inter-particle dipole-dipole interaction, causing characteristic spin-glass-like dynamics. A clear correlation between the blocking and freezing temperatures emerges from our studies for the first time.
CHAPTER 1
INTRODUCTION

Ferrofluids are stable colloidal dispersions of single domain magnetic nanoparticles in a liquid medium. Early studies of ferrofluids include those suspensions that settle out very slowly \[1\]. However, a true ferrofluid does not settle out completely, although a slight concentration gradient may build up after being subjected to gravitational or magnetic field over long periods of time. An aspect of this behavior is illustrated in Figure 1.1. Such ferrofluids are composed of solid, magnetic, single-domain particles of about 3-15 nm in diameter. The particles are often coated with an organic layer, which acts as a dispersant in the carrier liquid. Thermal agitation of the solid particles keep them suspended in the liquid through Brownian motion and the molecular coating prevents them from agglomerating. The earliest emergence of ferrofluids was in the form of “magnetic fluids”, which were introduced in the 1940s. Back then, micron-sized iron particles were mixed with clutch and brake oil for rheological investigations. As such, these were very different from present-day commercial ferrofluids made of nanometer-sized particles that remain homogeneously suspended in the liquid. In the early 60s, the study of ferrofluids steadily rose, fueled by the growing demand for a liquid material that can be strongly influenced by moderate magnetic fields. Such a material, enabling the control of its flow and physical properties over a wide range by means of a controllable magnetic force, was expected to give rise to numerous new applications like sealants in rotating shafts, voice-coil dampers in loudspeakers, hyperthermic agents in biomedicine, etc. A more detailed discussion of applications is provided below.

The primary challenge is that magnetic liquids do not exist in nature. All known ferromagnets have Curie temperatures far below their melting point. Hence, they lose their
ferromagnetic properties before turning liquid. An exception to this is the undercooled melts of Co-Pd alloys. But while this was found to show a magnetic phase transition [2], it is of no technical importance in terms of magnetic-field-controlled flows and related applications. Therefore, a completely new class of materials had to be developed to meet the necessities of the projected use of a magnetic fluid. The final breakthrough was made by S. Pappell’s success in producing stable suspensions of magnetic nanoparticles in carrier liquids [3]. These suspensions showed liquid behavior as well as superparamagnetic properties. This meant that minimal magnetic fields, which are comparable to gravitational forces, can affect the liquid. These suspensions eventually came to be called ferrofluids. Shortly after, the improved synthesis methods for ferrofluids motivated the development of fluids exhibiting long-time colloidal stability and reproducible properties. As time went by, concurrent to the improvements in the liquids themselves was the discovery of numerous other practical applications for ferrofluids, some of which have gained high commercial importance. Ferrofluids are now well-established as an important class of materials for
industrial applications. And this in itself warrants closer scrutiny of its physical properties. The prospect of biomedical applications for ferrofluids has further intensified this need to understand their physics at a fundamental level. These considerations constitute the underlying motivations of the present work.

1.1 Properties of Ferrofluids

Stability as a uniform suspension is an important property of ferrofluids that most commercial applications require. This stability is dictated mainly by the size of the particles, which need to be sufficiently small to prevent precipitation due to gravity. Charge and surface chemistry also contribute to stability by providing coulombic and steric repulsion. The critical size to maintain stability is estimated by considering the energies involved per particle, namely,

\begin{align*}
\text{thermal energy} & = k_B T \quad (1.1) \\
\text{magnetic energy} & = \mu_0 MH V \quad (1.2) \\
\text{gravitational energy} & = \Delta \rho V g L \quad (1.3) \\
\text{dipole-dipole contact energy} & = \mu_0 M^2 V \quad (1.4)
\end{align*}

where \( k_B \) is Boltzmann’s constant, \( \mu_0 \) is the permeability of free space, volume \( V = \pi d^3 / 6 \) for a spherical particle of diameter \( d \), \( \Delta \rho \) is the density difference between particles and carrier liquid and \( L \) is the elevation in the gravitational field or the typical height of a container.

The ratio between the thermal energy and magnetic energy gives the favorable size for stability against segregation:

\begin{align*}
\frac{\text{thermal energy}}{\text{magnetic energy}} & = \frac{\Delta \rho g L}{\mu_0 MH} \quad (1.5) \\
d & \leq \left( \frac{6kT}{\pi \mu_0 MH} \right)^{1/3} \quad (1.6)
\end{align*}
Interparticle interaction is present in a collection of small magnetic nanoparticles. Through thermal agitation, agglomeration among particles is prevented as long as the particle size is sufficiently small. This behavior is governed by the magnetic energy to gravitational energy ratio. The final requirement on colloidal stability that needs to be addressed is the stability against van der Waals attraction. The separation of bare magnetic particles in a carrier liquid cannot be guaranteed, since agglomeration due to van der Waals attraction will occur as soon as particles come into contact. To avoid irreversible agglomeration of the particles, they have to be prevented from coming into contact. As mentioned earlier, this is generally done by means of a surfactant layer consisting of long chain molecules with a polar head and a nonpolar tail [4]. The schematic diagram of a coated nanoparticle is shown in Figure 1.2. The polar head is attached to the particle’s magnetic core, while the tail reaches into the carrier liquid.

When a paramagnetic fluid is subjected to a sufficiently strong vertical magnetic field, the surface exhibits a normal-field instability. This effect is made manifest in the spontaneous formation of regular patterns of corrugations, as illustrated in Figure 1.3. The formation of the corrugations increases the surface free energy and the gravitational energy of the liquid, but reduces the magnetic energy. The corrugations will only form above a critical magnetic field strength, when the reduction in magnetic energy outweighs the increase in surface and gravitation energy terms. Ferrofluids have an exceptionally high magnetic susceptibility and the critical magnetic field for the onset of the corrugations can be released by a small bar magnet. With a fixed magnetic field, the concentration of the ferrofluid may be varied such that this effect becomes visible.

The most prominent property of ferrofluids is the change of viscosity due to an applied magnetic field. The first discovery of such changes was made by Rosensweig in 1969 [5] in concentrated magnetite-ferrofluids followed by the independent work of McTague [6] using highly diluted Co-ferrofluids. Both papers described an increase of viscosity of ferrofluids with increasing magnetic field strength and McTague’s experiments also showed a dependence of the effect on the relative angle between the magnetic field direction and
the vorticity of the flow. The first theoretical investigation of the phenomena was done by Shliomis [7] in 1972. It is assumed that the magnetic moment is fixed in the particle, i.e. the magnetic relaxation is governed by the Brownian relaxation. If a magnetic field is applied to the system, the magnetic moments of the particles will tend to align with the magnetic field direction. If the moment is fixed inside the particle as assumed above the rotation caused by the viscous friction will lead to a disalignment of magnetic moment and magnetic field. If the magnetic field is perpendicular to the vorticity of the flow, this will create a magnetic torque that will counteract the mechanical or viscous torque (see Figure 1.4) [8]. This magnetic torque hinders the free rotation of the particles, and produces an increase of the fluid’s viscosity. This increase is anisotropic, since it depends on the
Figure 1.3. A ferrofluid in a magnetic field showing normal-field instability caused by a neodymium magnet beneath the dish

mutual orientation of vorticity and magnetic field. Conversely, if the fluid’s vorticity is aligned with the field, the rotation of the particle will not force a disalignment of magnetic moment and field direction, and thus no magnetic torque will counteract the free rotation of the particles. Therefore no increase of viscosity will be observed.

Figure 1.4. Schematic diagram illustrating the origin of the field dependent increase of viscosity in a ferrofluid.

The movement of magnetic moment and particles in a ferrofluid may be described by the egg model [9]. The magnetic nanoparticle is the whole egg whose magnetic moment is situated at the yolk. Above the freezing temperature, the ferrofluid is in the liquid
Figure 1.5. The movement of magnetic moment and particles in a ferrofluid may be described by the egg model.

state and the particles are able to physically rotate in addition to the internal rotation of the spins inside the magnetic core. The green arrow in Figure 1.5 shows the rotation of the eggshell with the surrounding fluid of viscosity $\eta$ with angular velocity, $\omega_\eta$. This is characterized by the rotational diffusion relaxation time or the Brownian relaxation time given by

$$\tau_B = \frac{\pi D_{hyd} \eta}{2k_B T},$$

(1.7)

where $D_{hyd}$ is the hydrodynamic volume of the particles, $k_B$ the Boltzmanns constant and $T$ is the temperature. From the expression of relaxation time, it is seen that the Brownian mechanism strongly depends on the viscosity of the carrier liquid.

In the frozen state, however, particles are physically immobilized, which would ideally eliminate all contributions from Brownian relaxation. The magnetic moments may still undergo internal rotations with respect to the crystal axes. The yellow arrow represents
the rotation of yolk in the white with respect to the eggshell with angular velocity, $\omega_R$. This relaxes through the Néel mechanism given by Equation 1.8.

$$\tau_N = \tau_o \exp \left( \frac{KV_{mag}}{k_BT} \right),$$

(1.8)

where $\tau_o^{-1}$ is the Larmor frequency of the magnetization. $K$ is the effective anisotropy and $V_{mag}$ is the volume of the magnetic core, which collectively defines the activation energy (also denoted as $E_a$ in the latter chapters). The Néel mechanism strongly depends on the volume of the magnetic core.

1.2 Applications of Ferrofluids

When magnetic nanoparticles are dispersed in a carrier liquid, it forms a magnetic liquid or ferrofluids that are outstanding for several technological applications. Many applications are based on the special property of ferrofluids that they are attracted by magnetic field gradients while preserving their liquid character. Ferrofluids have capacity to withstand relatively high pressure and magnetic field gradients, hence, they are commercially being utilized as sealant for rotating shafts and as dampers in loudspeakers. Loudspeaker coils [10] consist of a cylindrical voice coil fitted to a cylindrical permanent magnet with a small gap that allows the coil to move. The heat developed in the voice coil can be dissipated rapidly when the air in the gap is replaced by a liquid. An ordinary liquid is unstable and would drip out, but a ferrofluid is retained by the magnetic field already present. Ferrofluids are also used in computer hard disk drives, for prevention against contamination [11] and as magnetic inks for jet printing [12], which are subjected to magnetic field gradients to deflect and position the ink droplets on the paper. The only disadvantage is that it takes longer time to dry on the paper. For magnetic reading of letters and numbers, e.g. on cheques, the magnetic properties of the dried ink are of outstanding importance. The paper is initially subjected to a magnetic field, before it is fed into the magnetic reader, so the dried ink must have a suitably high remanence for the letters to be read. Nowadays,
research is performed to influence the color of magnetic inks by building fluorescent dyes into the particles [11].

Another attractive aspect of ferrofluid research arises from the fact that they have been shown to exhibit interesting coupled magneto-mechanical effects when subject to different flow conditions and magnetic fields. This property has implications for novel energy conversion and power generation [13–17]. The basis for power generation arises from the well-known Faraday induction process which states that an emf is generated by time varying magnetic flux. In ferrofluids, one can think of the suspended nanoparticles as super-spins with high magnetic moments. Time variation of these moments caused by physical motion of the fluid with the particles combined with collective interaction among the particles would cause an induced emf in external pickup coils thus acting as a power source [18–20]. In the work of Gazeau et al. [13], they simultaneously measured the rotational viscosity and transverse susceptibility and depending on the ratio of the field frequency to the fluid vorticity, the particles behave as nano-motors or nano-generators. In addition, ferrofluids that are made to flow through capacitive membranes such as nanotubes would also be useful for energy conversion. Yang et al. [21] discussed the efficiency of microchannel arrays for electrokinetic battery applications.

With the advent of new synthesis techniques, it is now possible to make water-based magnetic suspensions that are important for biomedical applications. They are particularly useful for drug delivery, hyperthermia and contrast enhancement in MRI imaging. Ferrofluids have been shown to exhibit an incredibly high specific absorption ratio that is excellent for cancer therapy through hyperthermia [22, 23]. Heating between 41 °C and 46 °C can be induced by an AC magnetic field at frequencies up to 120 kHz, which is tolerable to humans. It has an advantage over heating of dried nanoparticles since the liquid medium facilitates homogeneous heating of the target tissue.

Other potential applications of ferrofluids are their use as optical devices, such as shutters, exploiting the change in transmittance of light upon alignment of the particles in a magnetic field. Here, small magnetic particles are needed to decrease the response time of
the shutter. A relatively new potential application is the use of a lattice of self-assembled monodisperse magnetic colloids in computers for data storage [24, 25]. However, new methods for writing and reading of data have to be developed first, to be able to use this in practice. Another very interesting application would be the use of magnetic colloids attached to catalysts, which could be separated after their use by means of magnetic field gradients. This application would then combine the advantages of homogeneous catalysis (high efficiency due to the large available surface) and heterogeneous catalysis (easy recycling of the catalyst).

1.3 Magnetic Properties of Nanoparticles

The understanding of the magnetic phenomena of various ferrofluids requires some knowledge of the nanoparticles that comprise the magnetic liquid. Magnetic nanoparticles show remarkable properties such as superparamagnetism, high field irreversibility, high saturation field. These are due to finite size and surface effects [26]. The two most studied finite size effects are the single domain limit and the superparamagnetic limit. It is well-known that larger magnetic materials are composed of uniformly magnetized regions called domains separated by domain walls. Domain wall formation is governed by the balance between the magnetostatic energy, which is proportional to the volume of the particle and domain-wall energy, which is proportional to the interface areas between domains. However, as predicted by Frenkel and Dorfman [27], for particles of a ferromagnet below a critical diameter, usually less than 15 nm, formation of domains is not energetically favorable. Such particles are said to be single domain. A single-domain particle is uniformly magnetized with all the spins aligned in the same direction and the mechanism for this is by spin rotation since there are no domain walls to move.

Another important phenomenon known as superparamagnetism is possible for these single-domain particles. This occurs when the thermal energy is enough to demagnetize the particle in the absence of an applied field. For an array of particles, it means that the net moment associated with each particle easily aligns with an applied field but is free
to rotate once the field is removed. This situation is analogous to a paramagnet, only instead of each individual spin aligning with the field and then randomizing after the field is removed, there are particles composed of roughly $10^5$ spins that can align with the field. This results in a much higher susceptibility and better magnetic response than a traditional paramagnet, but there is no coercivity or remanent magnetization.

To better understand this, we need to define another property called the magnetic anisotropy energy. The magnetic anisotropy energy per particle is the energy required for holding the magnetic moments along a certain direction. This is given by

$$E(\theta) = K_{eff} V \sin^2 \theta,$$

where $V$ is the particle volume, $K_{eff}$ is the anisotropy constant and $\theta$ is the angle between the applied field and the easy axis. The competition between the thermal energy, $k_B T$ and the energy barrier, $K_{eff} V$ determines the state of the spins. As the size of the particles decreases, the thermal energy dominates and the magnetization is easily flipped. This system is called a superparamagnet since there is now a giant spin inside each of the particle. The magnetic moment relaxes according to the Néel-Brown expression in Equation (1.10):

$$\tau = \tau_o \exp \frac{K_{eff} V}{k_B T},$$

If the particle magnetic moment flips at a time shorter than the measurement time scales, the system is in the superparamagnetic state. In general, magnetic nanoparticles can exhibit superparamagnetism only when the temperature is high enough to cause demagnetization by overcoming the anisotropy energy in the absence of a field. When the temperature is lowered and the thermal energy is not enough to demagnetize the particles, they again behave as single domain particles with magnetic hysteresis. Below this critical temperature, the magnetic moment reversal time is longer than the measurement time, and the system is said to be in the blocked state. The temperature that separates the two regimes is the blocking temperature, $T_B$ and it depends on the particle’s intrinsic properties.
and size. A simple and rapid way to estimate the $T_B$ is provided by the DC magnetization measurement, in which a zero-field cooled and field-cooled procedure is employed. This procedure is discussed in Section 3.1 and is further explained in Section 5.2.

The conditions given above for superparamagnetism all assume that the particles demagnetize due to thermal energy simultaneously with the removal of a field, and on the timescale of most DC measurements this appears to be true. However, there is a finite timescale for the particles to demagnetize, and when the magnetic properties are probed with an AC field, the blocking temperature can increase. Thus measurement frequency is also a factor when describing the blocking behavior of a superparamagnetic system. AC susceptibility measurements are especially useful for characterizing the timescales involved in superparamagnetic nanoparticles. As originally theorized by Néel and Brown [28], the particles are assumed to be noninteracting and the blocking temperature is given by

$$T_B = \frac{\Delta E}{\ln(\tau/\tau_o)k_B} \quad (1.11)$$

where $\Delta E$ is the energy barrier to magnetization reversal in a single particle, $\tau$ is the measurement time and $k_B$ is the Boltzmann constant. $1/\tau_o$ is called the attempt frequency and describes how fast a particle reverses its magnetization. Typically, this values fall in the range $10^{-10} - 10^{-9}$s. Rearranging the equation above yields the typical form of the Néel-Arrhenius relation:

$$\tau = \tau_o \exp \left( \frac{E_a}{kT} \right) \quad (1.12)$$

For weakly interacting particles, the systems behaves according to Vogel-Fulcher law:

$$\tau = \tau_o \exp \left( \frac{E_a}{k} \frac{1}{T_p - T_o} \right), \quad (1.13)$$

where $\tau$ is the relaxation time ($\tau = 1/f$; $f$ is the frequency), $\tau_o$ is the microscopic flipping time of the fluctuating spins, $E_a$ is the thermal activation energy, $T$ is the temperature,
and \( T_o \) is the characteristic temperature with thermal energy dominating for \( T > T_o \) and interaction energy for \( T < T_o \).

The best way to study the interaction effects on the dynamical behavior of nanoparticles is to measure the properties most sensitive to interactions, which are the frequency-dependent susceptibility and the time-dependent magnetic relaxation. As we will see in Chapter 5, both these models will be utilized in analyzing the relaxation peaks in the AC susceptibility. This allows us to determine the interaction regimes present in the ferrofluids.

This thesis presents a thorough magnetic characterization of nanoparticles and ferrofluids. The measurement of the magnetic properties of nanoparticles, particularly the magnetic anisotropy, was done using a nonconventional technique that is highly sensitive to interparticle interaction. Evidently, ferrofluids have been explored for several decades now. However, several aspects of its behavior are still not well-understood, owing to the complex nature of the system. Many of the earlier studies focused on one type of ferrofluid system in which either the nanoparticle size distribution or solvent remained the same and typically the particle volume fraction was varied to explore dipolar interaction effects. In this work, through systematic DC and AC susceptibility studies of different ferrofluids with different particle sizes in different solvents, we demonstrate that the physical origins of glass-like relaxation peaks are associated with the particle blocking and carrier fluid freezing effects. A clear correlation between the particle blocking temperature and the liquid’s freezing temperature is established for the first time.

The rest of the thesis is organized as follows: The next chapter discusses the synthesis of nanoparticles and preparation of the ferrofluids used in the study. Chapter 3 describes the traditional measurement techniques used in the magnetic characterization as well as the method of transverse susceptibility, which is a new technique to directly probe the anisotropy of a magnetic material. Chapter 4 focuses on the systematic study of the influence of interparticle interactions in nanoparticle assemblies directly on the anisotropy peaks. Chapter 5 is dedicated specifically to the discussion of ferrofluids where the physical origins of relaxation peaks and magnetic anomaly, which remained unclear in previous
works, are elucidated. Lastly, Chapter 6 concludes the thesis and proposes recommendations for future work. Our observations and results documented in detail in this thesis have also been presented in the following publications over the past few years [29, 30].
CHAPTER 2
SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NANOPARTICLES AND FERROFLUIDS

The method of synthesizing ferrofluids consists of (i) preparation of magnetic nanoparticles and (ii) the subsequent stabilization of the surfactant-coated nanoparticles in different nonpolar solvents. A wide variety of compositions and phases of magnetic nanoparticles, including iron oxides such as $\text{Fe}_3\text{O}_4$ and $\gamma$-$\text{Fe}_2\text{O}_3$ pure metals such as Fe and Co, spinel-type ferrites such as $\text{CoFe}_2\text{O}_4$, $\text{MnFe}_2\text{O}_4$, and $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, have been synthesized for several decades now. With the advent of new and efficient synthetic routes, it is now possible to fabricate shape-controlled, highly stable and monodisperse magnetic nanoparticles. Some of the popular methods including co-precipitation, microemulsion synthesis, and hydrothermal synthesis can all be employed to yield high-quality magnetic nanoparticles. Since this work is largely focused on the $\text{Fe}_3\text{O}_4$ system, chemical co-precipitation of $\text{Fe}_3\text{O}_4$ is discussed in detail in section 2.1. Other synthesis methods are described briefly in the following sections. For completeness, the procedure used by our collaborators for synthesizing manganese zinc ferrite is also outlined in Section 2.4.

Upon production of the ferrofluids, physical and structural characterizations are performed to verify the composition, shape and size of the nanoparticles. Results of the XRD scans and TEM images are also reported in this chapter.

2.1 Chemical co-precipitation of Iron Oxide Ferrofluids

Chemical co-precipitation is a facile and convenient route for synthesizing $\text{Fe}_3\text{O}_4$ from aqueous $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ salt solutions by addition of a base at elevated temperature. The entire procedure is performed under inert gas environment. There are two main methods
to precipitate predominantly spherical magnetite particles in solution. The first process was developed by Khalafalla et al. [31] and is outlined below.

*Scheme 1. Co-precipitation of iron salts.* The overall stoichiometry of this method is given in Equation 2.1.

\[ 5\text{NaOH} + 2\text{FeCl}_3 + \text{FeCl}_2 = \text{FeO} \cdot \text{Fe}_2\text{O}_3 + 5\text{NaCl} + 4\text{H}_2\text{O} \] (2.1)

In this reaction, Fe\(^{3+}\) and Fe\(^{2+}\) are in 2:1 molar ratio. Sodium hydroxide may be replaced by other basic solvent such as ammonium hydroxide. The procedure was carried out by dissolving in a reaction vessel (Figure 2.1) 1.988 g of FeCl\(_2\)-4H\(_2\)O and 5.406 g of FeCl\(_3\)-6H\(_2\)O in 20 ml water. As the mixture was being subjected to vigorous magnetic stirring under a flow of nitrogen, it was immediately heated to 80 °C. Upon reaching 80 °C, 5 ml of NH\(_4\)OH was added dropwise. This abruptly turns the solution black in color. The solution was allowed to reflux for 2 hours and then cooled down. Excess reactants may be discarded to extract the bare powder. The particles were further cleaned using ethanol followed by centrifugation and magnetic decantation. At this point, the Fe\(_3\)O\(_4\) nanoparticles have already formed. This recipe typically yields spherical nanoparticles with an average size of 10 to 15 nm. However, the as-synthesized Fe\(_3\)O\(_4\) at this stage is easily oxidized and becomes γ-Fe\(_2\)O\(_3\) (maghemite) upon exposure to air. In addition, the resulting particles are negatively charged and tend to agglomerate due to strong dipole-dipole interaction. For the purpose of several applications, formation of larger clusters is unfavorable as this does not retain good dispersion in host media or desirable nanomagnetic properties. It is necessary to perform an additional procedure to protect and stabilize magnetic nanoparticles against agglomeration. Typically, an efficient strategy to passivate the surface of the nanoparticles is the use of surfactant or polymer coating and redispersion in organic solvents. This process is called peptization. Peptization results in stable colloids. The procedure above was slightly modified such that 18 g oleic acid is added after cooling down the solution. The coated particles were then flocculated by neutralizing the solution using hydrochloric acid. The black product settles to the bottom in a neutral environment.
Figure 2.1. Three-necked reaction vessel used for ferrofluids synthesis. The long reflux condenser is connected through one of the inlets to conserve the volume of the solvent during reaction.

This allows the liquid to be separated from the precipitate through magnetic decantation. The particles were cleaned of excess surfactants by addition of ethanol and subsequent centrifugation at 6000 rpm for 5 minutes. The recovered particles were dissolved and stored in hexane.

A flow chart of the procedure described above is illustrated in Figure 2.2 [32]. An advantage of this scheme is that it is an economical way to prepare iron oxide nanoparticles in reasonably large quantities. However, there is limited control over the size of the particles and the procedure often yields polydisperse nanoparticles.

Scheme 2. Seed-mediated synthesis of monodispersed iron oxide nanoparticles. The second method is more flexible in terms of size tunability. The outcome is smaller diameter nanoparticles with narrow size distribution. In contrast to the previously described procedure, the surfactant is immediately added to the mixture and heated at higher temperatures along with the other reagents. This step encourages multiple tiny clusters to
nucleate simultaneously. The recipe follows closely the method described in Ref. [33]. Figure 2.3 shows the schematic representation of Scheme 2 co-precipitation of iron oxide preparation. To synthesize 6 nm size Fe₃O₄, the following reactants were combined in the reaction vessel: Fe (III) acetylacetonate (2 mmol) and 1,2-hexadecanediol (10 mmol) were added to 20 ml benzyl ether while stirring vigorously. The particles were coated with oleylamine (6 mmol) and oleic acid (6 mmol). The mixture was heated to 200 °C for 2 hours under argon environment and then allowed to reflux for 1 hour at 300 °C. After cooling down to room temperature, the resulting black mixture was washed by adding 40 ml of ethanol. The black precipitate was extracted after centrifugation and magnetic decantation. The nanoparticles were then dissolved in hexane containing 1 drop each of oleic acid and oleylamine to ensure that nanoparticles were fully coated. Fe₃O₄ nanoparticles were stored in hexane liquid.
To prepare the ferrofluids, measured amounts of the dried powder obtained by evaporation of carrier liquid were redispersed in hexane or any other organic solvent of choice.

Figure 2.3. Chemical co-precipitation method for preparing Fe$_3$O$_4$ ferrofluids

The particle size is varied by changing the amounts of solvent while keeping all the amounts of reagents the same. If the volume of benzyl ether is reduced to 15 ml, the resulting particles are 8 nm in size. Further reduction in solvent volume led to 15 nm Fe$_3$O$_4$. Another factor that affects the size of particles during synthesis is the amount of surfactant used. If 4 mmol of oleic acid and 4 mmol of oleylamine are mixed with 20 ml benzyl ether solvent, the average particle size is 9 nm. 12 mmol oleic acid and 12 mmol of oleylamine in 20 ml benzyl ether led to 5 nm. Changing the amount of benzyl ether to 15 ml does not seem to affect the size when only 4 mmol of oleic acid/oleylamine were used. The effect of solvent reduction is more evident in the presence of 6 mmol and 12 mmol oleic acid/oleylamine. These results are summarized in Table 2.1.

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<th>4 mmol</th>
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<td>10 ml</td>
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<td>20 ml</td>
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Table 2.1. Relationship between the size of Fe$_3$O$_4$ particles (in nm) and amount of surfactant (in mmol) or solvent volume (in ml)

The ratio of metal to surfactant was kept at 1:3 as prescribed by the recipe. According to literature, this particular ratio has been noted to yield monodisperse nanoparticles.
2.2 Synthesis of Cobalt Ferrite (CoFe$_2$O$_4$)

Synthesis of larger diameter CoFe$_2$O$_4$ is composed of a two-step process involving seed-mediated growth as described in Ref. [34]. The general strategy is using coordination compounds of iron(III) and cobalt(II) acetylacetonate, Fe(acac)$_3$ and Co(acac)$_2$, as precursors to synthesize spherical CoFe$_2$O$_4$ nanocrystals with a mean diameter of ~5 nm. The resulting 5 nm nanoparticles will be utilized as seeds to grow larger spherical particles.

The procedure is carried out as follows: 2 mmol of Co(acac)$_2$ is dissolved 40 ml of phenyl ether. 20 mmol of 1,2-hexadecanediol, 10 ml of oleic acid, and 10 ml of oleylamine was heated to 156 °C under Ar$^+$ gas environment and with vigorous magnetic stirring. At 156 °C, 4 mmol Fe(acac)$_3$ dissolved in 20 ml of a phenyl ether was added dropwise to the solution. The temperature was then increased quickly to 260 °C, which is the boiling point of phenyl ether. The mixture was allowed reflux for 30 min before being cooled down to room temperature. To clean the particles, ethanol is added followed by centrifuging at 9000 rpm for 5 minutes followed by 6000 rpm for another 5 minutes. This yielded spherical CoFe$_2$O$_4$ with a diameter of 5 nm.

To produce 9 nm CoFe$_2$O$_4$, 100 mg of 5 nm seeds was mixed with 1 mmol of Co(acac)$_2$, 2 mmol of Fe(acac)$_3$, 10 mmol of 1-octadecanol, 5 ml of oleic acid, and 5 ml of oleylamine. Then, the solution was quickly heated to 260 °C at a rate of 10-15°C/min and kept at reflux at 260 °C for 30 min. For the sample used in the study, some instabilities in the temperature control may have affected the growth. The temperature usually does not settle to the actual set point and often needs to be maintained manually. As a result, most of the reaction may have been carried out in a lower temperature, which encourages formation of larger particles. Several trials of the synthesis process were done and we have consistently produced sizes larger than 9 nm. CoFe$_2$O$_4$ ferrite synthesis exhibits more sensitivity to temperature gradients than Fe$_3$O$_4$ since the synthesis of the latter using the same temperature controller seems to be unaffected by this setback. Structural characterization of the precipitated nanoparticles using this procedure is reported in the next section.
2.3 Structural Characterization

X-ray powder diffraction (XRD) patterns of the particle assemblies were collected on a Bruker D8 Advance diffractometer under CuKα radiation ($\lambda = 1.5405\ \AA$). Samples for transmission electron microscopy (TEM) analysis were prepared by evaporation of a very dilute hexane ferrofluid on amorphous carbon-coated copper grids. The particles were imaged using a Morgagni 280 (100 kV) TEM. The XRD pattern of the Fe$_3$O$_4$ nanopowders prepared using Scheme 1 is shown in Figure 2.4. From the plot, we can see that the indexed peaks are consistent with the cubic spinel structure of Fe$_3$O$_4$. From a histogram analysis of the TEM image in the inset of Figure 2.4, the average particle size was estimated as 14±3 nm. The TEM micrographs shows that the nanoparticles are spherical in shape and polydispersed. Figure 2.5 shows the structural characterization of Fe$_3$O$_4$ prepared using...
Figure 2.5. Powder x-ray diffraction profile of the dried ferrofluid indexed with the \((hkl)\) reflections of the cubic Fe\(_3\)O\(_4\) phase. Upper left panel: selected area from TEM images of Fe\(_3\)O\(_4\) nanoparticles. Upper right panel: histogram of the particle sized populations as observed from TEM images.

Figure 2.4. The size of the particles obtained from the TEM image (inset) is found to be 6 nm ± 2 nm. The histogram is also presented in the same figure. The broad distribution is consistent with the polydisperse quality of the sample.

The XRD pattern for the CoFe\(_2\)O\(_4\) nanoparticles is shown in Figure 2.6. The peaks observed are consistent with the spinel structure of CoFe\(_2\)O\(_4\). Spherically shaped nanoparticles were precipitated from the seed-mediated growth described in the previous section as seen from the TEM micrograph in Figure 2.7. The mean diameter is 11 nm ± 3 nm.

2.4 Synthesis of Manganese Zinc Ferrite (MZFO) by Reverse Micelle Method

The other nanoparticle system presented in this research were synthesized by collaborators. Manganese zinc ferrite (MZFO), was received from S. Morrison and E. Carpenter.
Figure 2.6. Powder x-ray diffraction profile of the dried ferrofluid indexed with the \((hkl)\) reflections of the spinel \(\text{CoFe}_2\text{O}_4\) phase.

Figure 2.7. Transmission electron micrograph of 11 nm spherical \(\text{CoFe}_2\text{O}_4\) nanoparticles.

from the Virginia Commonwealth University. Monodisperse MZFO nanoparticles with an average size of 15 nm were synthesized using a versatile reverse-micelle technique. To synthesize by reverse micelle method, two reverse micellar solutions were prepared, the first is the stock solutions of 0.5 M sodium dioctylsulfosuccinate (AOT) prepared in 2,2,4-
trimethylpentane (isooctane) and the second was an aqueous metal solution prepared by combining 0.045 M FeCl$_2$, 0.0176 M MnCl$_2$, and 0.0176 M ZnCl$_2$. The two solutions are combined under constant stirring. The reaction was allowed to proceed for 2 h. Particle flocculation was induced by addition of excess methanol. To collect the particles, methanol was added to the solution followed by centrifugation. This step removes excess surfactant. The particles were further cleaned by a methanol:water solution to remove any additional unreacted ions. After final centrifugation, the material was dried overnight under a dynamic vacuum, and subsequently fired at 525 °C for 5 h under flowing nitrogen.

The stoichiometry of each sample was determined to be Mn$_{0.68}$Zn$_{0.25}$Fe$_{2.07}$O$_3$. Powder x-ray diffraction confirmed the single phase and crystallinity of the material. The full synthesis details and characterization results are found in Ref. [35].
CHAPTER 3
MAGNETIC MEASUREMENT TECHNIQUES

All magnetization measurements in this work were performed in our laboratory using a Physical Properties Measurement System (PPMS) from Quantum Design. The PPMS shown in Figure 3.1 consists of a liquid helium dewar equipped with a longitudinal superconducting magnet, which can give a field up to ±7 Tesla. The temperature can be varied in the range 2K to 450K. Magnetization versus field (M-H curves), magnetization versus temperature (M-T) and AC susceptibility measurements were all performed using a built-in probe of the PPMS, the AC/DC Magnetometry System (ACMS). The transverse susceptibility measurements were performed using tunnel diode oscillator (TDO), which is a resonant circuit integrated with a custom-built probe that fits into the PPMSS. The different magnetic characterizations, such as DC magnetization, AC susceptibility and RF susceptibility are discussed in the following sections.

3.1 DC Magnetization

The magnetic properties of a material are commonly probed by the application of an external DC field. One of the most important DC magnetic measurements is the magnetization versus field or the hysteresis loop. A number of quantities can be determined from the hysteresis loop, namely the saturation magnetization $M_S$, remanent magnetization $M_R$, and coercive field $H_C$. Each of these quantities are indicated in a sample graph shown in Figure 3.2 and are defined as follows. One starts with a material in an unmagnetized state, $M = 0$. This is immersed in a magnetic field, $H$, that is gradually increased from zero field in some arbitrary positive direction. The magnetization, $M$, increases from zero to $M_S$. After saturation, the magnetic field is reduced and the $M_S$ decreases to $M_R$, which is the
remanent or residual magnetization. The reversed field required to decrease the magnetization to zero is called the coercivity, $H_C$. The field is then brought to negative saturation and then back to the positive maximum field to close the loop. Most materials, except those that exhibit exchange bias, have the same magnitude of $H_C$ both in the positive and negative saturation. Materials that have high $H_C$ and high $M_R$, which results in an open loop, are said to be hard magnets. Superparamagnetic nanoparticles, on the other hand, show no coercivity above the blocking temperature and depending on the nanoparticle system, low temperature coercivity is in the range of $\sim$500 Oe to $\sim$10000 Oe.

The shape of the hysteresis loop implies the suitability of the material to a particular application. For example, a square-shaped loop with large remanence and coercivity are suitable for data storage since it has two stable magnetic states. These states can represent the 1s and 0s in binary logic. On the other hand, M-H loops with very small coercivity

![Figure 3.1. Physical Properties Measurement System (PPMS).](image-url)
Figure 3.2. Magnetization versus field curve of a ferromagnetic material.

are characteristic of soft magnetic materials and are useful in transformer cores and other AC and RF applications. By observing the M-H loop, soft and hard magnets may be distinguished from one another. Soft magnets are characterized by a narrow loop with small coercivity. If the loop is narrow, it is suitable for transformer core application since the polarization is easily changed with a small field. M-H loops can also have shapes determined by the geometry and intrinsic magnetic anisotropy.

We also characterize our samples by measuring the temperature dependence of the magnetization in two different conditions: first the material is cooled in the absence of a field to obtain the zero-field cooled (ZFC) curve and second in the presence of an external DC field to obtain the field-cooled curve (FC). This type of measurement is especially useful for determining the average blocking temperature, $T_B$, of nanoparticles. A sample ZFC-FC curve of a nanoparticle system composed of Fe$_3$O$_4$ powder is shown in Figure 3.3. To measure ZFC curve, the sample is initially cooled to a temperature as low as 5 K with $H = 0$. When low temperature is achieved, a small constant field of about 100 Oe is applied and the magnetization, $M_{ZFC}$ is taken during the warming cycle. At room temperature, the nanoparticles are randomly oriented and the effective magnetic moment is
Figure 3.3. Zero field cooled (ZFC) and field cooled (FC) magnetization versus temperature curves for Fe$_3$O$_4$ nanoparticles.

zero. When the nanoparticles cool down, they become frozen in a random state. Then the field is applied but none of the moments are able to align in the frozen state so $M_{ZFC}$ is practically zero. As the temperature increases, some moments unfreeze and align with the external field and $M_{ZFC}$ increases. It will continue to increase until thermal fluctuations of the nanoparticles are strong enough to demagnetize the sample. The temperature at which the nanoparticles changes from the ferromagnetic phase to superparamagnetic phase is the blocking temperature and it appears as a peak in the ZFC curve.

On the other hand, the FC measurement is obtained by cooling the sample in the presence of an external field. The moments of the nanoparticles being easily magnetized, instantly align with the field. As the temperature decreases to freezing temperature, the nanoparticle moments become frozen randomly with the moments on average aligned in the field direction. The DC field remains as the measurement is taken in the warming cycle. $M_{FC}$ starts at a finite value having all moments aligned in the direction of the field. It begins to fall off as the temperature increases and the moments physically fluc-
tuate in the superparamagnetic state. Similar to superparamagnetic nanoparticles, the ZFC-FC magnetization measurement is a standard method to study spin-glass systems, which are primarily disordered magnets. A peak in the $M_{ZFC}$ curve is typical of both superparamagnetic nanoparticles and spin-glasses. However, a minimum is observed in $M_{FC}$ at low temperature only for spin glass. The peak of $M_{ZFC}$ agrees qualitatively with the freezing temperature. This can be obtained quantitatively from the AC susceptibility measurements, which will be discussed in the next section.

### 3.2 AC Susceptibility

In AC magnetic measurements, a small oscillating magnetic field is applied causing a time-dependent moment in the sample. The field of the time-dependent moment induces a current in the pick-up coils, allowing measurement without sample motion.

At low frequencies where the measurement is comparable to a DC measurement, the magnetic moment of the sample follows the M-H curve that would be measured in a DC experiment. As long as the AC field is small, the induced AC moment is given by

$$M_{AC} = \chi \times H_{AC} \sin(\omega t) \quad (3.1)$$

where $H_{AC}$ is the amplitude of the driving field, and $\omega$ is the driving frequency. $\chi = dM/dH$ is the susceptibility as well as the slope of the M(H) curve at very small fields where the magnetization is still reversible. $H_{AC}$ is usually around 10 Oe where the susceptibility is still in the linear regime. One advantage of AC susceptibility is that the measurement is very sensitive to small changes in magnetization. Since the AC measurement is sensitive to the slope of M(H) and not to the absolute value, small magnetic shifts can be detected even when the effective moment is large.

At higher frequencies, the AC moment of the sample does not follow along the reversible part of the DC magnetization curve due to dynamic effects in the sample. Essentially, the rotation of the magnetic moment cannot keep up with the alternating magnetic field. In
this higher frequency case, the magnetization of the sample may lag behind the drive field, an effect that is detected by the PPMS using mutual inductance circuitry. Thus, the AC magnetic susceptibility (often known as the dynamic susceptibility) measurement yields two quantities: the magnitude of the susceptibility, \( \chi \), and the phase shift, \( \phi \), relative to the drive signal. Alternatively, one can think of the susceptibility as having an in-phase, or real, component \( \chi' \) and an out-of-phase, or imaginary, component \( \chi'' \). The two terms are related by

\[
\chi' = \chi \cos \phi \quad \text{(3.2)}
\]

\[
\chi'' = \chi \sin \phi \quad \text{(3.3)}
\]

\[
\chi = \sqrt{\chi'^2 + \chi''^2} \quad \text{(3.4)}
\]

In the limit of low frequency where the AC measurement is not different from the DC measurement, the real component \( \chi' \approx \chi \) as discussed above. The imaginary component, \( \chi'' \), indicates dissipative processes in the sample. In ferromagnets, a nonzero imaginary susceptibility can indicate irreversible domain wall movement or absorption due to a permanent moment. Also, both \( \chi' \) and \( \chi'' \) are very sensitive to thermodynamic phase changes, and are often used to measure transition temperatures.

AC susceptibility measurements are especially useful for characterizing superparamagnetic nanoparticles. As originally theorized by Néel and Brown [28], the particles are assumed to be noninteracting and the blocking temperature is given by

\[
T_B = \frac{\Delta E}{\ln(\tau/\tau_0)k_B} \quad \text{(3.5)}
\]

where \( \Delta E \) is the energy barrier to magnetization reversal in a single particle, \( \tau \) is the measurement time and \( k_B \) is the Boltzmann constant. \( 1/\tau_0 \) is called the attempt frequency and describes how fast a particle reverses its magnetization. Typically, this values fall in
the range $10^{-10} - 10^{-9}$s. Rearranging the equation above yields the typical form of the Néel-Arrhenius relation.

$$\tau = \tau_o \exp \left( \frac{E_a}{kT} \right) \quad (3.6)$$

The peaks observed from graphs of both $\chi'$ and $\chi''$ correspond to the blocking temperature at the transition from ferromagnetism to superparamagnetism. Since $T_B$ depends on the measurement frequency, the peak in $\chi''$ vs. $T$ occurs at different temperatures for different frequencies. From such measurement, one can check that the particles are truly noninteracting by verifying the dependence of $T_B$ on measurement time as given by the Neel-Brown theory. Departures from this theory indicate interparticle interactions, for example dipole-dipole or interparticle exchange interactions. The frequency dependent peak in $\chi''$ vs. $T$ exhibited by superparamagnetic particles is a characteristic similar to spin glasses. However, spin glasses show a cooperative phase transition while superparamagnets show a gradual blocking of particles. Take note that the Néel-Arrhenius relation is limited to the magnetization reversal of a non-interacting single domain particle over an anisotropy barrier, $E_a$. In Chapter 5, we discuss the origin of the glass-like peaks observed in the AC susceptibility measurement of ferrofluids.

### 3.3 RF Susceptibility

Transverse susceptibility ($\chi_T$) is measured by taking the magnetic susceptibility in one direction while an external magnetic field is oriented perpendicular to the direction of measurement. Measurement of $\chi_T$ is useful in a direct determination of magnetic anisotropy. The anisotropy field of a material is the field needed to saturate the magnetization of a material in the hard direction and is related to the effective anisotropy $K_{\text{eff}}$ through the equation:

$$H_K = 2K_{\text{eff}}/M_s \quad (3.7)$$
Directly measuring the anisotropy field of a material by transverse susceptibility is very useful in comparison with other methods.

The underlying principle of transverse susceptibility is described in a classic theoretical paper by [36], Aharoni et al. in 1957. They calculated $\chi_T$ as a function of $H_{DC}$ for so-called Stoner-Wohlfarth particles [37], which are ellipsoid, single domain ferromagnetic particles with uniaxial anisotropy. According to Aharoni’s theory, measurement of $\chi_T$ with respect to $H_{DC}$ applied perpendicular to the easy axis of magnetization should yield three cusps corresponding to the positive and negative anisotropy fields, $\pm H_K$ and the switching field, $H_S$. The theoretical plot in Figure 3.4 (extracted from the original paper) shows both the transverse and parallel susceptibility as the field is changed from positive to negative saturation.

![Figure 3.4](image)

Figure 3.4. Theoretical transverse susceptibility ($\chi_T$) and parallel susceptibility ($\chi_P$) curves as a function of reduced field $h$ ($h = H_K/H_{DC}$) as calculated by Aharoni et al. Figure adapted from reference [36].

In order to measure transverse susceptibility we use a self-resonant RF frequency technique based on a tunnel diode oscillator (TDO) instead of a standard susceptometer. This technique was developed by Srikanth, et al. [38] and was first tested on a manganese per-
ovskite sample. It is composed of an LC tank circuit powered by a tunnel diode biased in its negative resistance region and is resonant at 12 to 15 MHz. The field generated by the coil may be oriented parallel or perpendicular to the variable external DC field provided by the solenoid of PPMS magnet and we can independently resolve the parallel and transverse components of susceptibility. This circuit is incorporated in a modified multifunction probe that could be inserted in the sample chamber of the PPMS.

The LC tank circuit operates at a frequency given by

\[ \omega = \frac{1}{\sqrt{LC}} \]  

(3.8)

When a sample is inserted into the inductive coil, there is a small change in the coil inductance \( \Delta L \). If \( \Delta L/L << 1 \), one can differentiate Equation 3.8 and obtain the expression

\[ \frac{\Delta \omega}{\omega} \approx -\frac{\Delta L}{2L} \]  

(3.9)

Any change in inductance is related to the change in the susceptibility of the material. The inductance coil in this experimental setup serves as the sample space in which a gel cap containing the sample can fit. This entire coil is inserted into the sample chamber of our PPMS using a customized radio frequency (RF) co-axial probe. The schematic diagram of the TDO probe is shown in Figure 3.5.

The DC magnetic field \( (H_{DC}) \) is varied using the PPMS. The oscillating RF field \( H_{RF} \) produced by the RF current flowing in the coil, is oriented perpendicular to \( H_{DC} \) and this arrangement sets up the transverse geometry described in the previous section. When \( H_{RF} \) is perpendicular to the varying \( H_{DC} \), the change in inductance is actually determined by the change in transverse permeability \( \mu_T \) of the sample. Thus, we can derive an absolute value for the transverse susceptibility \( \chi_T = \mu_T - 1 \). The percent change in transverse susceptibility then can be defined as

\[ \frac{\Delta \chi_T}{\chi_T} (%) = \left| \frac{\Delta \chi_T(H) - \chi_T^{sat}}{\chi_T^{sat}} \right| \times 100 \]  

(3.10)
where $\chi_T^{sat}$ is the transverse susceptibility at the saturating field $H_{sat}$. Data acquisition is controlled by a Labview program by specifying the magnitude of the saturating field in Oe units and the sampling rate in Oe/sec. The program protocol initially saturates the sample to the maximum positive field then reduces the field to zero. The field crosses over zero to negative saturation field. From this field, the scan retraces its path to zero field and finally terminates as the positive saturation field. The outcome of each run is a bipolar scan of the susceptibility as a function of the field that has all the features necessary for extraction of anisotropy and switching fields.

Over the years, this technique has been proven by our group to be an excellent probe of magnetic anisotropy of bulk, thin films and nanoparticles. Since this is a resonant method, we are able to use the high degree of sensitivity ($\Delta \chi \approx 10$ Hz in a resonance of 10 Mhz) to measure samples even with very weak moments that are difficult to be directly picked up by conventional magnetometry. Transverse susceptibility measurements using TDO is useful in a variety of applications. In this work, we utilize transverse susceptibility measurements
in directly probing the dipolar interactions in nanoparticle assemblies. The results of this study are discussed in Chapter 4.
CHAPTER 4
STATIC AND DYNAMIC MAGNETIZATION OF NANOPARTICLES

In studying the magnetic properties of nanoparticles, standard measurements such as DC magnetization and AC susceptibility are typically done. In this chapter, a new technique of characterizing nanoparticles is discussed. This nonconventional way of measuring the magnetic properties, particularly magnetic anisotropy, has been used by our group in studying magnetic bulk and thin film systems and is found to be useful even for nanoparticles in a three dimensional assembly. The results of the standard DC and AC measurements are also presented.

One of the most important properties of magnetic materials is the magnetocrystalline or magnetic anisotropy. Magnetic anisotropy is the intrinsic energetic preference of ferromagnetic moments to align along an easy direction of magnetization. The magnetic anisotropy energy is the energy involved in rotating the magnetic moment from an easy axis to another direction (hard axis). Different degrees of magnetic anisotropy is desired in different applications, such as permanent magnets, information storage devices, recording/read heads and biomedicine. Therefore, it is important to study the effect of various factors on a material’s anisotropy. In fact, recent research efforts in magnetically anisotropic materials for media storage at higher densities have demanded the requirement for experimental techniques that can directly probe the magnetic anisotropy and its temperature dependence in a precise manner.

There exist several approaches to measure the magnetic anisotropy in fine magnetic particle systems. Examples include the saturation approach, the torsional pendulum, rotational hysteresis, remanent-torque magnetometry, complex permeability spectra, etc. but
most of these techniques are indirect and often unwieldy for extracting information about the anisotropy [39–48]. For example, in the saturation approach, to get the anisotropy constant, one has to do M-H measurements along the hard axis direction and extrapolate the effective anisotropy from the slope change in field-dependent magnetization. However, this is difficult in aggregates of magnetic nanoparticles due to the uniaxial symmetry for spherical particles and distribution in preferred axis directions [44, 45]. Recently, magnetic force microscopy has been shown to yield information about the anisotropy of individual hemispherical nanoparticles grown onto a substrate [49]. This method, while excellent for determining anisotropy distribution and orientation, is limited to room temperature. Transverse susceptibility (TS), which is a singular point detection technique, has been reasonably successful in assemblies of polycrystalline single-domain particles in probing the anisotropy field in the presence of particle size distribution and texturing (orientation of easy axes) [39, 40].

Despite a wealth of literature being available on measurements and modeling of magnetic anisotropy using the transverse susceptibility (TS) technique, only very few studies present systematic measurements of the effect of interparticle dipolar or exchange interactions on the effective anisotropy peaks. Portions of this chapter can be found in Ref. [29] where we have described how transverse susceptibility measurement can be a very powerful tool in directly probing the effect of interparticle interactions in nanoparticles. This work represents the first correlation of anisotropy peak behavior with interparticle interaction.

4.1 Experimental Details

The high quality manganese zinc ferrite (MZFO) nanoparticles used are highly monodispersed and coated with surfactant. To study the effect of varying strength of dipolar interactions on TS peaks in a reasonably controlled fashion, we varied the concentration of the nanoparticles embedded in wax. We used paraffin wax since it is magnetically benign and does not interfere in any magnetic measurement. The coated particles were first dispersed in propanol. Three samples labeled as MZFO (50), MZFO (100), MZFO (500) were prepared
by adding 50, 100, 500 µl of suspension, respectively in same amount of molten paraffin wax. The presence of excess surfactant prevented agglomeration of the particles and we let the wax solidify under sonication to ensure that the particles are randomly distributed all throughout the wax matrix. And then a fourth sample, MZFO-concentrated (MZFO-conc) was prepared by simply drying out the solvent without any wax. The variation in coercivity and blocking characteristics as observed through dc susceptibility experiments were measured and compared with TS experiments described in the previous chapter.

4.2 DC Characterizations

DC characterization results in Figure 4.1 show the M-H loop comparing MZFO (50), MZFO (100), MZFO (500) and MZFO (conc) samples. The blocking temperature can be identified by the sharp transition in the curves. As seen from the graph, the blocking temperature increases for increasing concentration. The sharpness of the peak indicates the narrow distribution of the particle size, otherwise, a broad transition is observed. This would also mean that the wax does not facilitate agglomeration of the particles in contrast to media such as polymers used in several studies. It has been shown that the normal tendency of particles in polymer matrices is to agglomerate because of the strong steric forces and their effect on the magnetic properties could be easily observed [50]. In a previous study, we have shown how this agglomeration of the nanoparticles in polymers can be overcome using careful choice of solvent and surfactant mixtures but these complications are not present in paraffin wax used in this study so we do not need special procedures.

Figures 4.2 and 4.3 shows the comparison of the M-H loops of all the samples at 300 K and 10 K, respectively. The curves at 300 K confirms the superparamagnetic state of the nanoparticles showing reversible behavior and zero coercivity. At 10 K, a systematic increase in the coercivity with increasing packing fraction (from 144 to 192 Oe) can be seen which clearly shows an effect of interparticle interaction strength. This increase in coercivity is consistent with increase in the blocking temperature. The values are of the blocking temperature and coercivity for all the samples are summarized in Table 4.1.
4.3 Transverse Susceptibility (TS) as a Tool to Probe Interparticle Interactions

We discuss here the results of the transverse susceptibility measurements taken at different temperatures. The samples were first zero-field cooled and each curve was obtained while warming up. At each temperature, we did a bipolar scan from positive saturation to negative saturation and then back to positive saturation. We could identify the two anisotropy peaks, $H_{K1}$ (positive) and $H_{K2}$ (negative). And from these plots we can see how the anisotropy peaks evolve with increasing temperature. We have shown representative TS curves for samples MZFO(100) and MZFO(conc) in Figures 4.5 and 4.4. The family of curves (composed of bipolar scans) traces the evolution of the system as the temperature is increased. As can be noticed in these figures, when the temperature is lowered, the single peak in the TS at zero field splits into two peaks, which become more prominent with decreasing temperature and shift to higher field values. It is also clear from Figures 4.5...
and 4.4 that the overall shape of the TS curves including the peak positions is remarkably different for the two extreme cases of MZFO(conc) and MZFO(100). To follow these differences in features in the TS closely, we have compared in Figure 4.6 the unipolar scans (from positive saturation to negative saturation) for different samples at four fixed temperatures.

In Figure 4.7, we have plotted the peak position versus temperature curves for all the four samples in both the positive and negative field (of the unipolar scan). The peak positions are almost symmetric to each other and strongly dependent upon temperature. Again from the curves in Figure 4.6, it can be observed that at 15 K, the peaks corresponding to MZFO (conc) are situated at larger field values in comparison the other samples [MZFO (conc) > MZFO (500) > MZFO(100) > MZFO(50)]. This shows that the values of effective anisotropy peak positions, as obtained from TS curves, are strongly affected by interparticle dipolar interactions and increases with the strength of the interparticle interaction strength. Our experimental results are thus in contrast to earlier theoretical studies that predicted a decrease in the anisotropy fields with enhanced interactions [51–53].

Another important feature of TS curves is the height and shape of the TS peaks located at $\pm H_K$. As observed from Figure 4.6, in the TS experiments, when going from positive saturation to the negative saturation field values, $H_{K1}$ is always larger than $H_{K2}$. This is a fact that we have consistently observed in our previous studies as well [50, 54–56]. However,
it was unclear what causes the difference in the height of the peaks and the systematic studies here on samples of varying interaction strengths allows us to explore the origin of the peak height symmetry. To better express the issue of peak height quantitatively, in Figure 4.8, we have plotted the peak height difference,

\[
\text{Peak height difference} = \frac{(\text{Peak height})_{HK1} - (\text{Peak height})_{HK2}}{(\text{Peak height})_{HK1}} \times 100\%
\]  

(4.1)

as a function of sample temperature. It is remarkable to see that the concentrated sample, the peak height difference is highly reduced in comparison to the weakly interacting particle system. Our results indicate that the difference in peak heights (located at \( \pm H_K \), or the asymmetry, is also extremely sensitive to a change in the dipolar interaction strength and increases with decreasing interaction. In a recent theoretical investigation by Matarranz et al. [53] it was claimed that for a textured assembly of uniaxial single-domain interacting particles, the dispersion in the anisotropy field (particle size, shape) causes the
peak height asymmetry and broadening. They calculated that that for a monodispersed assembly of particles, the TS peaks would be very sharp and similar in height. However, our experimental study is in sharp contrast to this and the trend is the opposite. Note that in our case we have taken particles from the same synthesis batch and all other experimental conditions remain the same for all the samples except for the concentration of the particles in wax that determines the interparticle interactions. Therefore, we infer that the anisotropy field dispersion remains constant for all the samples. We also conclude that the change in the peak height difference is not due to the distribution of the anisotropy field alone as indicated by previous theoretical studies but the interparticle interaction also plays a major role. Overall, we demonstrate that TS is sensitive enough to pick up small changes in the interaction strength. We now present arguments that will help qualitatively understand the evolution of the peak height asymmetry from large to small as the nanoparticle system goes from weakly to strongly interacting cases. To explain this, recall that the sample was first saturated at a positive field and $H_{K1}$ always occurs after saturation,
when the Zeeman energy is highest. Since the particles are largely affected by the changing field, the rotation of the moments is more coherent causing a sharper peak with a higher magnitude at $H_{K1}$. When the field crosses zero, the moments have essentially randomized. At this point, the inter-particle interactions are dominating the magnetic response. Hence, for weakly interacting particles, the response in the randomized state will be much smaller even if the applied field is increased. As a result, we observe $H_{K2}$ to be of smaller height. Conversely, strongly interacting particles should result to more symmetric peaks since the field each particle experiences from its neighbors should have a similar response to an applied field. A decrease in Zeeman energy should not have as large an effect on the collective response of the system. Thus, in general, when the field is reversed in polarity, the height and width of the second peak on the negative side are different for the two cases (i.e., small and broad for the case of noninteracting particles versus larger and sharper for the case of interacting particles) and depends on the different energy landscapes seen by the non-interacting and interacting particles at zero field (demagnetized state). This explains the TS peaks being symmetric in height for samples with strong interactions and displaying a large asymmetry for noninteracting/weakly interacting particles. Our explanation is also very consistent with TS data on ferromagnetic thin films which always display sharp peaks symmetric in height [57, 58].
Figure 4.4. Representative transverse susceptibility curves for MZFO(conc) sample.
Figure 4.5. Representative transverse susceptibility curves for MZFO(100) sample.
Figure 4.6. Comparative view of transverse susceptibility curves at various concentrations and temperatures.
Figure 4.7. Peak position ($H_K$) versus temperature curves in both the quadrants for various concentrations. The field positions of the anisotropy peaks in (presented as I for the positive field and II for the negative field) as a function of temperature.

Figure 4.8. Anisotropy peak height difference (arbitrary scale) versus temperature curves at various concentrations.
In the previous chapter, we have seen the magnetic properties of nanoparticles embedded in a solid wax matrix. We now investigate the magnetic response when magnetic nanoparticles are dispersed in a carrier liquid. Ferrofluids, which have extensive potential in technological applications, as discussed in Chapter 1, are excellent model systems for studying the magnetic characteristics and relaxation phenomena in magnetic nanoparticles [8, 59–66]. When the magnetization of a ferrofluid is measured over a range of temperature, unlike in a wax matrix, we are able to examine nanoparticles while they are in a liquid as well as in a solid environment. The dynamics that occur at the transition from liquid to solid as the ferrofluid is cooled down and enters a frozen state are likewise accessible.

It has been shown that the magnetic properties of ferrofluids are dominated by the dipole-dipole interaction between the suspended particles [59]. Particle size distribution [60], concentration [61, 62], and surfactant coating [63] as well as solvent used in the suspension [64] all affect the dipole-dipole interaction [59], which in turn give rise to the range in magnetic behavior observed [65, 66]. Despite a number of previous studies [67–69], however, the understanding of the physical origin of the magnetic anomalies [66] and relaxation phenomena [65] in ferrofluids remains unclear in part due to the complex nature of the system and also the fact that many of these earlier studies focused on one type of ferrofluid system in which either the nanoparticle size distribution or solvent remained the same and typically the particle volume fraction was varied to explore dipolar interaction effects. In particular, Luo et al. [65] reported their observation of the two characteristic peaks in the temperature-dependent complex susceptibility ($\chi = \chi' - i\chi''$) in Fe$_3$O$_4$-based ferrofluids, but the origin of these peaks remained unknown. They demonstrated via
differential scanning calorimetry (DSC) measurements that there exist three characteristic states (e.g. liquid, mixed and frozen states) in a ferrofluid or a solvent. For temperatures above the pour point \( T_{\text{pour}} \) a liquid phase exists as the system flows like a fluid, whereas a solid phase (or a frozen state) is present at low temperatures below \( T_{s-m} \), and a mixed phase exists in the temperature range between \( T_{s-m} \) and \( T_{\text{pour}} \), where \( T_{s-m} \) is the transition temperature from the solid phase to the mixed phase. Importantly, the first peak in \( \chi'' \) (at high temperature) has been found to belong to the temperature range of \( T_{s-m} < T < T_{\text{pour}} \) (in the mixed state), while the second peak in \( \chi'' \) (at low temperature) to the frozen state. Therefore, the difference in the relaxation mechanism between these two peaks is attributed to the difference in the magnetic behaviors between the frozen and mixed states of a ferrofluid. When investigating the magnetic properties of Fe\(_3\)O\(_4\)-based ferrofluids, Zhang et al. [66] observed a glass-like cusp (at high temperature) and magnetic anomaly (a drop in magnetization at low temperature) in the zero-field-cooled (ZFC) magnetization. However, the origin of these features also remained unclear. In review of these two cases, we note that the occurrence of a glass-like cusp and magnetic anomaly in the ZFC curve [66] is associated with the existence of the two relaxation peaks in the \( \chi''(T) \) curve [65], and that the effects of particle blocking and solvent freezing must play a role in governing the observed phenomena.

In this work, through systematic experimental studies and comparative analysis on different types of ferrofluids, we reveal for the first time, a remarkable correlation between particle blocking and carrier fluid freezing that plays a critical role in understanding the physical origin of the magnetic anomalies in ferrofluids. We attempt to clarify the effect of particle blocking on the magnetic characteristics in each of the three states (e.g. liquid, mixed and frozen states) and demonstrate that the blocking effect plays a significant role in establishing the magnetic behavior in the mixed and frozen states, but not in the liquid state.
5.1 Ferrofluid Samples

Fe$_3$O$_4$ and CoFe$_2$O$_4$ nanoparticles were synthesized using the chemical synthesis technique described in Chapter 2. Structural characterizations were also discussed in Section 2.3. The mean particle sizes were 14 nm ± 3 nm and 6 ± 2 nm for Fe$_3$O$_4$ and 11 nm ± 3. For the dispersing liquids, hexane and dodecane were chosen since they have the same composition but differ in room temperature viscosity and melting points. Dodecane, having a longer hydrocarbon chain than hexane, has a viscosity of 1.35 cP (centipoise) and freezes at 264 K. Hexane, on the other hand has a viscosity of 0.294 cP and a freezing temperature of 177 K. The volume concentrations were kept almost the same for all the samples investigated (~2 vol%). For clarity, we will use the following labels in the rest of the chapter to refer to specific samples: Sample FP (Fe$_3$O$_4$ in dry powder form), Sample FH (Fe$_3$O$_4$ in hexane), Sample FD(Fe$_3$O$_4$ in dodecane), Sample CP (CoFe$_2$O$_4$ in dry powder form), Sample CH (CoFe$_2$O$_4$ in hexane) and Sample CD (CoFe$_2$O$_4$ in dodecane).

5.2 Anomaly in DC Magnetization

We measured magnetization versus field curve for the dry powders of Fe$_3$O$_4$ and CoFe$_2$O$_4$ at 10 K and 300 K. From the M-H curves in Figures 5.1 and 5.2, we find that at 300 K, there is no hysteresis whereas the loops at 10 K exhibit a clear hysteresis with a coercivity of around 150 to 200 Oe for Fe$_3$O$_4$. CoFe$_2$O$_4$ has a low temperature coercivity of 1900 Oe. This is characteristic of the sample being superparamagnetic at room temperature and entering a blocked state at low temperature which results in opening up of the hysteresis loop. The general observations are consistent with that reported in a paper by us [70] and other authors [66, 71] on Fe$_3$O$_4$ and CoFe$_2$O$_4$ nanoparticles.

The ZFC and FC magnetization curves taken at 100 Oe for 14 nm Fe$_3$O$_4$ and 11 nm CoFe$_2$O$_4$ are shown in Figures 5.3 and 5.4. The top panels in both figures correspond to the powder samples FP and CP, the middle panels are for hexane ferrofluids, FH and CH and the bottom panels are for dodecane ferrofluids, FD and CD. It can be observed in
Figure 5.1. Magnetization versus field curve for Fe$_3$O$_4$ nanoparticles taken at 10K and 300K.

Figure 5.2. Magnetization versus field curve for CoFe$_2$O$_4$ nanoparticles taken at 10 K and 300 K.
Figures 5.3(a) and 5.4(a), that the ZFC curve exhibit the typical blocking process of an assembly of superparamagnetic Fe$_3$O$_4$ (CoFe$_2$O$_4$) particles with a distribution of blocking temperatures at $T_B \sim 200$ K ($\sim 212$ K). Recall that to determine $T_B$ in the ZFC curve, the sample is first cooled down in zero field from a high temperature (300 K) to a lowest measured temperature ($T_o$), at which the total magnetization of the sample is zero since the magnetic moments of particles are randomly oriented. On heating the sample, the application of a magnetic field, H, induces a net magnetic moment along the magnetic field direction, which will increase with increasing temperature in the range $T_o < T < T_B$ as more and more particles become unblocked and reach their equilibrium ($T \sim T_B$). However, with further increase in temperature ($T > T_B$), the net moment of the particles that are already superparamagnetic decreases and follows a Curie law as a function of temperature [71]. As a result, a peak appears to occur in the ZFC curve, and this peak temperature is the average $T_B$ for the whole sample.

Figure 5.3. ZFC-FC curves for 14 nm Fe$_3$O$_4$ samples (a) Fe$_3$O$_4$ powder (FP) (b)Fe$_3$O$_4$+hexane (FH), (c)Fe$_3$O$_4$+dodecane (FD).
The behavior described above is very different from that of ferrofluids. Figure 5.3(b) and (c) show the ZFC and FC curves for sample FH and FD, respectively. The ZFC curves exhibit a sharp peak in samples FH and CH, while a small peak followed by the magnetic anomaly (i.e., the sharp drop in the ZFC magnetization at low temperature) are observed for samples FD and CD. We note, herein, that the $T_B$ of the Fe$_3$O$_4$ and CoFe$_2$O$_4$ magnetic nanoparticles, 200 K and 212 K, respectively are above and close to the freezing temperature($T_F$) of hexane (177 K), whereas the blocking temperatures of both magnetic nanoparticles is much lower than the freezing temperature ($T_F$)of the solvent dodecane (264 K). This clear distinction in the samples allows us to attribute the observed peak and magnetic anomaly in Figure 5.3(c) and 5.4(c) to the freezing effect of the solvent and the blocking effect of magnetic nanoparticles, respectively. Importantly, we find that
the magnetic anomaly is only observed in ferrofluids having \( T_B < T_F \) (i.e. for dodecane ferrofluids).

In contrast, for the ferrofluids having \( T_B > T_F \), the ZFC-FC magnetization in the liquid state \( (T > T_F) \) is not affected by the particle blocking but for the ferrofluids having \( T_B < T_F \) the blocking effect on the magnetic behavior is significant in the mixed and frozen states. Refer to Figures 5.3(a) and (c) and Figures 5.4(a) and (c) for comparison. It is the blocking effect in the frozen state that causes a sharper change in the ZFC magnetization at temperatures just below the freezing temperature for samples FH and CH when compared with the data in samples FD and CD. Therefore, for the ferrofluids having \( T_B > T_F \), the peaks at 186 K and 189 K are ascribed to the combination of both the blocking and freezing effects, whereas only the freezing effect contributes to the peaks at 270 K for sample FD and 272 K for sample CD for the ferrofluids having \( T_B < T_F \).

To summarize the results discussed so far, we highlight one of the remarkable features in ferrofluids. When nanoparticles are dispersed in a liquid, the freezing temperature of the ferrofluids increases. This is a common feature in liquids when particles are added. Dispersing in a liquid also causes the blocking temperature to decrease because particle separation becomes larger. In the case where the particles get blocked before the liquid freezes, as in hexane, an increase in the freezing, at the same time a decrease in blocking temperature results in a coincidence of the two peaks to a single sharp peak in the ZFC curve. In the case of ferrofluid with dodecane, the freezing temperature of the liquid is higher than the blocking temperature of the magnetic particles. This results in two distinct peaks corresponding to the freezing temperature and blocking temperature. This is what we refer to as the magnetic anomaly and it only occurs for the case of the dodecane ferrofluid. Thus our observation clarify the origin of these features for the first time even though they were observed by other groups in the past.

These results shed light on the physical mechanisms behind the spin-glass-like cusp and magnetic anomaly reported in the ZFC magnetization in ferrofluids, and provide important clues for assessing the complex nature of the glassy states in ferrofluids [59, 67, 72–75].
The idea is to tune the blocking temperature with respect to the freezing temperature of the solvent and this can be achieved in two ways. One option is to keep the particle size fixed for a given nanoparticle system and change the dispersing liquid. The second method is by varying size of the particles for a given solvent and nanoparticle system. The latter gives a better flexibility in terms of the range of blocking temperatures. To examine the effect of particle size, similar experiments were done on 6 nm Fe$_3$O$_4$ nanoparticles. The graph on Figure 5.5 shows the ZFC-FC curves for the samples containing 6 nm nanoparticles, denoted as 6FP, 6FH, 6FD. The blocking temperature of the Fe$_3$O$_4$ powder is at 35 K, which is far below freezing of both hexane and dodecane. Since the nanoparticles are small and well dispersed, the freezing peak is not visible and only a single peak due to the particle blocking effect is seen. These results clearly indicate that the blocking and freezing effects are particle-size dependent. The analysis of the AC susceptibility data in the next section will clearly show that the change in particle size affects the interparticle interaction, and in turn, categorizes the two sizes to different interaction regimes.

5.3 Origin of Spin Glass-like Relaxation Peaks

We now attempt to correlate the physical origin of the two peaks in the AC complex susceptibility observed [65] to the peak and magnetic anomaly in the ZFC DC magnetization [66] that remained unexplained by other groups. Figures 5.6, 5.7, 5.8 and 5.9 show the real part, $\chi'$, and imaginary part, $\chi''$, of the AC susceptibility as a function of temperature taken at different frequencies. As the frequency increases, the blocking temperature peaks in both $\chi'$ and $\chi''$ shift to higher temperature. To analyze this further, we focused on the peaks in the $\chi''$ versus $T$ plots as they are sharper and more pronounced. The collection of the graphs for $\chi''$ is shown in Figure 5.10. As seen in the figure, the $\chi''(T)$ curves show a single peak for the ferrofluids having $T_B > T_F$ (samples FH and CH), while two distinct peaks are observed for the ferrofluids having $T_B < T_F$ (samples FD and CD). The excellent correlation between features in the DC and AC magnetization is best revealed by combining the ZFC curve and the low frequency measurement of the AC susceptibility in a
Figure 5.5. ZFC-FC curves for 6 nm Fe₃O₄ samples.

single plot as in Figure 5.11. Here, one can infer that the second peak in $\chi''(T)$ is ascribed to the blocking of magnetic nanoparticles, while the first peak in $\chi''(T)$ is associated with the freezing of the solvent. As one can also see clearly in the combined plot that the first peak reflects the magnetic behavior in the mixed state, while the second peak represents the magnetic behavior in the frozen state. Our new findings allow us to correctly classify the two peaks in $\chi''(T)$ corresponding to the glass-like peak and magnetic anomaly as due to freezing and blocking for the Fe₃O₄ ferrofluids with kerosene solvent reported previously by Luo et al. [65] and for Fe₃O₄ ferrofluids with hexane solvent reported by Zhang et al. [66]. Note that it is only our comparative analysis between ferrofluids with varying blocking and freezing temperatures that leads to this clarification of the origin of the peaks and the conclusion would not be apparent just by looking at the data on one type of ferrofluid alone as in the case of the past studies.
5.4 Fits to Néel - Arrhenius and Vogel - Fulcher Relations

To probe the magnetization dynamics in these states, we examine the peaks in the \( \chi''(T) \) plots. The peaks observed from graphs of both \( \chi' \) and \( \chi'' \) correspond to the blocking temperature at the transition from frozen state to superparamagnetism. Since \( T_B \) depends on the measurement frequency, the peak in \( \chi'' \) vs. \( T \) occurs at different temperatures for different frequencies. From such measurement, one can check that the particles are truly noninteracting by verifying the dependence of \( T_B \) on measurement time as given by the Neel-Brown theory. Departures from this theory indicate interparticle interactions, for example dipole-dipole or interparticle exchange interactions. The frequency dependent peak in \( \chi'' \) vs. \( T \) exhibited by superparamagnetic particles is a characteristic similar to spin glasses. However, spin glasses show a cooperative phase transition of moments while superparamagnets show a gradual blocking of particles. Take note that the Néel-Arrhenius relation is limited to the magnetization reversal of a non-interacting single domain particle over an anisotropy barrier, \( E_a \).
AC susceptibility peaks observed at different temperatures can be fitted to different theoretical models to extract parameters inherent to the sample. Well-known models such as Néel-Arrhenius and Vogel-Fulcher relations are widely used for fitting data. The Néel-Arrhenius is valid for non-interacting particles and can be fitted by two parameters. On the other hand, Vogel-Fulcher model describes a system of weakly interacting particles and requires three parameters. The Vogel-Fulcher relation is given by Equation (1.13), where \( \tau \) is the relaxation time, \( E_a \) is the activation energy, \( k \) is the Boltzmann constant, \( T_p \) are the peaks from the graph of \( \chi'' \) and \( T_o \) is the interaction energy. For fitting the data, it is more convenient to express the relation in Equation (1.13) in terms of the frequency as in Equation (5.1) where \( \tau = 1/f \) was used. Here, \( f_o \) is the attempt frequency.

\[
\ln f = \ln f_o - \frac{E_a}{k} \left( \frac{1}{T_p - T_o} \right) \\
(5.1)
\]
By making a plot of $T_p$ versus $ln(f)$ and performing a nonlinear curve fitting, $\tau$, $E_a/k$ and $T_o$ were determined. The result of dipolar interactions is to slow down the attempt frequency because the particles must also overcome the local energy present from neighboring particles. However, as mentioned before, this relation is only valid for interacting nanoparticle systems, and at times would yield unphysical values. In that case, the third parameter, $T_o$ is set to zero to fit the Néel-Arrhenius model given by Equation 3.6.

For the ferrofluids investigated, the peak in $\chi''(T)$ shifts to higher temperature as the measurement frequency is increased (Refer to Figure 5.10) indicative of glassy behavior [76]. The glassy nature in ferrofluids is reasonably complex as contribution to the glassy states in the mixed and frozen regions results from the combined blocking and freezing effects [65, 73–75]. To clarify the blocking and freezing effects on the glassy behaviors in the mixed and frozen sates, we analyze the frequency dependence of the peaks of $\chi''(T)$ Figure 5.10, by fitting the data using both Néel-Arrhenius (NA) model in Equation 3.6 and Volgel-Fulcher (VF) scaling law in Equation 1.13.
Our results reveal that the $\chi''(T)$ data can be fit using Equation 3.6, but the fitting parameters obtained are unphysical, similar to the case reported in earlier references. This suggests that these ferrofluids belong to the class of interacting particle systems for which the Néel-Arrhenius model is invalid [77]. For our ferrofluids, the VF model has been found to fit well the $\chi''(T)$ data with acceptable fit parameters and the results are shown in Figure 5.12. The best fits for sample FD yield acceptable values for $\tau_o$, $E_a/k$ and $T_o$. The actual values are summarized in Table 5.1. Note that peaks in $T_{P1}$ are in the mixed state and $T_{P2}$ are in the frozen state. The difference in $\tau_o$ and $E_a/k$ for the cases of $T_{P1}$ and $T_{P2}$ indicates that for the ferrofluid having $T_B < T_F$, the glassy behavior is different

$$
\begin{array}{cccc}
T_{P1} & T_{P2} \\
\tau_o & (1 \pm 0.3) \times 10^{-7} \text{ s} & 1.8 \pm 0.4) \times 10^{-6} \text{ s} \\
E_a/k & (1.4 \pm 0.5) \times 10^2 \text{ K} & (4.5 \pm 0.4) \times 10^2 \text{ K} \\
T_o & 232 \text{ K} & 149 \text{ K}
\end{array}
$$

Table 5.1. Best fit values of $\tau_o$, $E_a/k$ and $T_o$ from VF relation for Fe$_3$O$_4$ in dodecane (FD)
in nature between the mixed and frozen states. This is understandable as the magnetic particles are unblocked in the former case, whereas they are already blocked in the latter case. The larger values of $\tau_o$ and $E_a/k$ for the case of $T_{P2}$ indicate that the blocking effect of magnetic nanoparticles on the glassy behavior in the frozen state is simply to cause slowing down of the dynamics of the system. In addition, we find that $T_o = 232$ K for the case of $T_{P1}$ which coincides with the temperature at which the ferrofluid enters into the frozen state from the mixed state and this transition is the origin of the divergence in the viscosity of the ferrofluid, whereas the divergence of the relaxation time at $T_o = 149$ K for the case of $T_{P2}$ suggests that the system enters a glassy state at this temperature. In view of these results, we propose that the blocking of magnetic nanoparticles in the frozen
state significantly affects the interparticle dipole-dipole interaction, causing characteristic spin-glass-like dynamics. This is in agreement with the previous studies on the influence of dipolar-dipolar interaction on the low-temperature magnetically glassy behavior and spin dynamics in frozen ferrofluids, which indicate that blocked moments are observed for the isolated particles (in a diluted ferrofluid) owing to a finite measurement time whereas the magnetic moments of the interacting particles (in a concentrated ferrofluid) freeze cooperatively as seen in a spin glass system [74, 75]. This also allows one to reconcile the observations of spin-glass-like states, magnetic relaxation and aging effect reported in the literature for ferrofluids [59, 65–67, 72, 75].

We now turn to clarify the difference in magnetically glassy nature between the mixed and frozen states in ferrofluids, with particle moments in the blocked state in both regimes, through studying the magnetically glassy characteristics of sample CH and sample CD. We note that the peak in $\chi''(T)$ for CH reflects the magnetic behavior in the mixed state ($T_{P1}$),
The best fits of $T_{pour}(f)$ data to the VF model extracted from AC susceptibility of Sample FD (for the cases of $T_{P1}$ and $T_{P2}$), Sample CH and Sample CD, while the second peak in $\chi''(T)$ for CD reflects the magnetic behavior in the frozen state ($T_{P2}$). Refer to Figures 5.10(c) and (d). The fitting results are also shown in Figure 5.12. The best fits for CH and CD yield values for $\tau_0$, $E_a/k$ and $T_o$ typical for CoFe$_2$O$_4$ systems. The values are summarized in Table 5.2

\begin{table}[h]
\centering
\begin{tabular}{ccc}
\hline
 & CH ($T_{P1}$) & CD ($T_{P2}$) \\
\hline
$\tau_0$ & $(1.3 \pm 0.4) \times 10^{-6}$ s & $(4 \pm 1) \times 10^{-6}$ s \\
$E_a/k$ & $(1.6 \pm 0.2) \times 10^2$ K & $(2.6 \pm 0.5) \times 10^2$ K \\
$T_o$ & 151 K & 173 K \\
\hline
\end{tabular}
\caption{Best fit values of $\tau_0$, $E_a/k$ and $T_o$ from VF relation for samples CH and CD}
\end{table}
The slight difference in $\tau_o$ and $E_a/k$ for these two samples indicates that the glassy nature between the mixed and frozen states are almost the same if the magnetic nanoparticles are already blocked in these states. The discrepancy here can arise from the difference in the viscosity of the solvents used, that is hexane or dodecane. A recent paper on the general dynamics of nanoparticles in supercooled liquids suggests complex organization of the particles due to hyperdiffusivity in the vicinity of the glass transition of the carrier fluid [78]. It is the larger value of the viscosity of dodecane (1.35 cP) in sample CD that results in the larger values of $\tau_o$ and $E_a/k$ for this sample when compared to sample CH (hexane: 0.294 cP). This indicates that the viscosity of the solvent also plays a role in the magnetically glassy behavior in the ferrofluids. This finding is important from the technological application perspective since the application of a magnetic field to a ferrofluid is shown to significantly change its viscosity that in turn modifies the magnetic behavior of the ferrofluid [8, 10]. Apart from this, we note that the difference in $\tau_o$ between CH and CD, $\tau_o = (1.8 \pm 0.4) \times 10^{-6}$ s (refer to Table 5.2) and $\tau_o = (4 \pm 1) \times 10^{-6}$, respectively, arises from the difference in particle size ($\sim$14 nm for Fe$_3$O$_4$ and $\sim$11 nm for CoFe$_2$O$_4$)
and their magnetic properties. The higher value of \( T_o \) of CD (173 K) compared to that of CH (149 K) suggests a stronger interparticle dipole-dipole interaction in this sample [77]. This agrees with the trend that the dipole-dipole interaction increases the characteristic relaxation time (\( \tau_o \)) of a particle system [79]. Our comprehensive studies on DC magnetization, AC susceptibility and previous works [74, 75, 78, 80, 81] on magnetic relaxation and aging phenomena provide evidence of the existence of a low temperature spin-glass-like phase in ferrofluids, but we should distinguish this phase from that observed in traditional spin glasses [76]. In ferrofluids the magnetic moment of a magnetic nanoparticle is several orders larger than atomic moments in spin-glass materials. The time needed for spin flipping of magnetic nanoparticles (\( \tau_o \sim 10^{-6} \)) is thus much longer compared with that of an atomic spin (\( \tau_o \sim 10^{-13} \)), and it depends exponentially on the particle size [79, 82]. As a result, in ferrofluids even a small distribution of the particle size can give a broad range of relaxation times [78, 80, 81], contributing partially to the observed glassy phenomena.

The samples containing smaller nanoparticles were analyzed in a similar fashion. For the 6 nm Fe\(_3\)O\(_4\) samples, the data were found to best fit the Néel-Arrhenius relation and not the Vogel-Fulcher model. The best fit curves for samples 6FP, 6FH, 6FD, are shown in Figure 5.13. Values of the parameters extracted from the best fits are summarized in Table 5.3. From these values, it is clear that the relaxation time is faster for ferrofluids involving high viscosity liquids such as dodecane.

<table>
<thead>
<tr>
<th></th>
<th>6FP</th>
<th>6FH</th>
<th>6FD</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_o )</td>
<td>((1.69 \pm 0.4) \times 10^{-10} ) s</td>
<td>((2.07 \pm 0.5) \times 10^{-11} ) s</td>
<td>((1.25 \pm 0.6) \times 10^{-11} ) s</td>
</tr>
<tr>
<td>( E_a/k )</td>
<td>((5.11 \pm 0.6) \times 10^2 ) K</td>
<td>((3.34 \pm 0.2) \times 10^2 ) K</td>
<td>((4.22 \pm 0.1) \times 10^2 ) K</td>
</tr>
</tbody>
</table>

Table 5.3. Best fit values of \( \tau_o \), \( E_a/k \) and \( T_o \) from Néel-Arrhenius relation for 6 nm Fe\(_3\)O\(_4\) samples

Table 5.4 summarizes the results of the ZFC and AC studies discussed indicating whether or not the magnetic anomaly is present in each of the samples. We can see
Table 5.4. Tabulated results for the ZFC and AC studies of all ferrofluid samples. NA denotes Néel-Arrhenius and VF denotes Vogel-Fulcher.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_B$</th>
<th>ZFC</th>
<th>AC</th>
<th>Anomaly</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>14FH</td>
<td>$T_B &gt; T_F$</td>
<td>sharp peak</td>
<td>single peak</td>
<td>absent</td>
<td>NA</td>
</tr>
<tr>
<td>14FD</td>
<td>$T_B &lt; T_F$</td>
<td>two peaks</td>
<td>two peaks</td>
<td>visible</td>
<td>VF</td>
</tr>
<tr>
<td>11CH</td>
<td>$T_B &gt; T_F$</td>
<td>sharp peak</td>
<td>single peak</td>
<td>absent</td>
<td>VF</td>
</tr>
<tr>
<td>11CD</td>
<td>$T_B &lt; T_F$</td>
<td>two peaks</td>
<td>two peaks</td>
<td>visible</td>
<td>VF</td>
</tr>
<tr>
<td>6FH</td>
<td>$T_B &lt; T_F$</td>
<td>single peak</td>
<td>single peak</td>
<td>absent</td>
<td>NA</td>
</tr>
<tr>
<td>6FD</td>
<td>$T_B &lt; T_F$</td>
<td>single peak</td>
<td>single peak</td>
<td>absent</td>
<td>NA</td>
</tr>
</tbody>
</table>

that the double peak feature denoting the presence of magnetic anomaly only occurs for ferrofluids containing large diameter nanoparticles and in highly viscous medium.

5.5 Frequency Dependence of the AC Susceptibility

Finally, we present and discuss the relaxation mechanisms in the frozen and mixed states by investigating the frequency dependence of the complex susceptibility. Figure 5.14 and its inset show the $\chi'(f)$ curves at three different temperatures for two representative ferrofluids (sample FH and sample CD). To explain these results, we first recall that both Brownian and Néel relaxations have been observed in ferrofluids [62, 64, 83–85]. At room temperature, the ferrofluid is in the liquid state and the particles are able to physically rotate in addition to the internal rotation of the spins inside the magnetic core. The loss component of the complex AC susceptibility ($\chi''$) will show two peaks with the low frequency peak corresponding to Brownian relaxation and the high frequency peak ascribed to the combination of Brownian and Néel relaxations. They also appear as two distinct slopes in the in-phase ($\chi'$) or gain component of the frequency-dependent susceptibility. In the frozen state, physical motion of the particles is arrested, which would ideally cause the low frequency loss peak to disappear. In addition, the second peak shifts to lower frequency with an attenuated amplitude. In this case, $\chi'$ would also monotonically decrease with frequency exhibiting a single slope. In terms of these analyses, we consistently note that for ferrofluids having $T_B > T_F$, a double slope feature in $\chi'(f)$ is observed in the mixed state which evidently indicates coexistence of both Brownian and Néel relaxation in this
state, while $\chi'(f)$ shows only a linearly monotonic decrease in the frozen state, signifying the presence of only Néel relaxation. For the ferrofluids having $T_B < T_F$ (the inset of Figure 5.14), the non-monotonic, double slope feature in $\chi'(f)$ is observed at temperatures above $T_B$ but in the frozen state, and $\chi'(f)$ only shows a linear feature as the temperature is lowered below $T_B$. This indicates the presence of Brownian relaxation in addition to Néel relaxation even in the frozen state. This trend seen in our samples is consistent with the recent observation that thermal motion of magnetic nanoparticles in ferrofluids continues well below the freezing temperature of the solvent or in the frozen state [62].

![Graph](image)

Figure 5.14. Real part of magnetic susceptibility, $\chi'$, as a function of frequency of Sample FH in the mixed state (at 177 K and 185 K) and in the frozen state (at 165 K). The inset shows the $\chi'(f)$ curves of Sample CD in the mixed state (at 230 K and 255 K) and in the frozen state (at 185 K).
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

The achievements of this research may be summarized as follows:

We have investigated the influence of increasing dipolar interactions on the blocking temperature, coercivity, and the magnetic anisotropy in monodispersed manganese zinc ferrite nanoparticles. Transverse susceptibility has been used to directly probe the effect of inter-particle interactions on the anisotropy and it is observed that the anisotropy fields increase with increasing interactions. The asymmetry in TS peaks is also associated with the strength of interactions with weakly interacting particles exhibiting strong asymmetry in the TS anisotropy peaks whereas they are symmetric for strongly interacting particles.

We have established for the first time a correlation between the blocking temperature of magnetic nanoparticles ($T_B$) and the freezing temperature of the solvent ($T_F$) in ferrofluids. This correlation allows one to explain the physical origins of relaxation peaks in the complex susceptibility and the spin-glass-like cusp and magnetic anomaly in the zero-field-cooled magnetization in ferrofluids. It is demonstrated that the magnetic anomaly is observed for ferrofluids having $T_B < T_F$ but not for ferrofluids having $T_B > T_F$. The blocking effect of magnetic nanoparticles plays a significant role in establishing the magnetic behavior in the mixed and frozen states, but not in the liquid state. In the frozen state the blocking effect of magnetic nanoparticles significantly affects the interparticle dipole-dipole interaction, causing spin-glass-like slow dynamics. The viscosity of the solvent also plays a role in the magnetically glassy behavior in the ferrofluids. In the frozen state both Néel and Brown relaxations coexist for ferrofluids having $T_B < T_F$, but for ferrofluids having $T_B > T_F$ only Néel relaxation is present.
We have demonstrated that the particle blocking and carrier liquid freezing effects are important to the formation of the glass-like relaxation peaks in ferrofluids. These effects are particle-size dependent. The freezing effect of the carrier liquid on the magnetization dynamics of ferrofluids containing larger magnetic nanoparticles is more pronounced than that containing smaller magnetic nanoparticles. Even though ferrofluids have been studied for decades and they are used in several technological applications, our results in this research indicate subtle interplay between the particle size effects and carrier fluid properties. Thus these two properties can be suitably tuned to produce engineered ferrofluids for specific applications.

Extreme cases of non-interacting and interacting particle systems have been reported in this work and the properties of ferrofluids containing nanoparticles of intermediate size (∼10 nm) are currently being explored. Moreover, the effect of varying the nanoparticle concentration in ferrofluids and performing transverse susceptibility susceptibility measurements are being considered for future work.

Ferrofluids that exhibit a very sharp peak in the $M$ vs. $T$ curve are potentially useful in magnetic refrigeration applications. The basis of this is that the sharp transition indicates a large entropy change, which is a common feature of magnetocaloric materials. The ongoing work on magnetocaloric materials in our laboratory would enable us to consider exploration of these phenomena in ferrofluids. We have also recently added a heat capacity probe to our PPMS. This would open up new research avenues for future students in the laboratory in terms of studying the thermomagnetic properties of ferrofluids.

Future work on ferrofluids may be extended to biological samples to improve magnetic resonance imaging (MRI) contrast and hyperthermia for tumor therapy. Preliminary work on hyperthermia studies that has been done include synthesis of water-based ferrofluids and setting up of a room temperature experiment for measuring dissipative heating. The synthesis techniques described in this thesis were modified to make biocompatible ferrofluids. Iron oxide nanoparticles were coated using either citric acid or polyethylene glycol (PEG) to enable them to suspend in water. Another scheme that was employed was to convert
oil-based ferrofluids to water-based ones. This has been carried out by the author using controlled amounts of block copolymer, particularly Pluronic 157, dissolved in water and mixed with the as-synthesized nanoparticles stored in a volatile organic solvent. From this procedure, very stable suspensions were produced. Shelved for almost a year and flocculation in these ferrofluids has not been observed. Such ferrofluids are excellent for biomedical applications such as hyperthermia cancer treatment. A room temperature experiment has been setup to measure the energy dissipated through relaxation of the superparamagnetic nanoparticles. It is a simple setup that makes use of hand-wound coils and the only major component of the setup is the source of the external AC magnetic field coupled with an amplifier that operates up to 120 kHz. The main challenge is to achieve heating up to 46 °C using an AC field of 120 kHz or less as operating frequency and minimal amplitude. It is also important to determine the optimal size of the nanoparticles than will generate such energy.
REFERENCES


Appendix A List of Publications

Journal Articles


Conference Proceedings

Appendix A (Continued)

Appendix B List of Conference Presentations

Conference Presentations


