MAGNETO-OPTICAL AND RHEOLOGICAL BEHAVIORS OF OIL-BASED FERROFLUIDS AND MAGNETORHEOLOGICAL FLUIDS

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MAGNETO-OPTICAL AND RHEOLOGICAL BEHAVIORS OF OIL-BASED FERROFLUIDS AND MAGNETORHEOLOGICAL FLUIDS

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Dissertation

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The magneto-optical and rheological behaviors of magnetic fluids and magnetorheological (MR) fluids have been investigated. A magneto-optical apparatus was constructed which enabled us to investigate the birefringence and dichroism of ferrofluids at various levels of applied magnetic field. Specifically, the effects of the film thickness of oil-based ferrofluids and the concentration of surfactant in the oil-based ferrofluids on their magneto-optical behavior were investigated. A commercial magneto-rheological instrument (Physica MCR 301, Anton Paar) equipped with a cone-and-plate fixture was employed to investigate the transient and steady-state shear flow of both ferrofluids and MR fluids as a function of shear rate at various levels of applied magnetic fields. The rheological investigation has enabled us to determine the effect of applied magnetic field on the shear viscosity and yield stress of ferrofluids and MR fluids. A special ferrofluid was prepared by filtering out nearly all of the surfactant and small particles in an oil-based ferrofluid. We then compared its magneto-optical and rheological behaviors with those of an unfiltered ferrofluid. Further, we have found that the ferrofluid with a lower concentration of surfactant gave rise to larger birefringence and yield stress, and stronger shear thinning behavior than the ferrofluid containing a higher concentration of surfactant. This observation has lead us to conclude that an increase in unbound surfactant in a ferrofluid hindered chain formation of magnetic particles, leading to a decrease in the optical and rheological behaviors of the ferrofluid.
Optical microscopy confirmed no visible chain formation of magnetic particles in the ferrofluid having a high concentration of surfactant owing to weak yield stress, birefringence, and shear thinning. On the other hand, we observed from optical microscopy that the filtered ferrofluid gave rise to larger yield stress, birefringence, and stronger shear thinning behavior. Thus, using optical microscopy we were able to explain the magneto-optical and rheological behaviors of the ferrofluids and magnetorheological fluids investigated.
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Magnetism is caused by the ordered alignment of electrons in an atom. If we consider each electron as an infinitesimally small magnetic dipole, then the vector representing the strength and direction of the dipole is the magnetic moment. Magnetization is defined as

\[ M = (V/N)m \]

where \( V \) is the volume of the material, \( N \) is the number of magnetic particles, and \( m \) is the magnetic moment of the particles.

The different types of magnetization a material can have are graphically shown in Figure 1.1. All materials are diamagnetic. The hallmark of diamagnetic materials is that they are linear (defined as \( M = \chi H \) where \( M \) is the magnetization, \( H \) is the applied magnetic field, and \( \chi \) is the magnetic susceptibility) and they have a \( \chi < 0 \).

Paramagnetism is a special case of diamagnetism where \( \chi > 0 \). The other type of magnetization (which is a special case of paramagnetism) is called collective magnetization. Collective magnetization differs from para and diamagnetization in that it is no longer linear (\( M \neq \chi H \)) since for collective magnetization there is a residual magnetization (\( M \)) of the material under no applied field (\( H \)). Collective magnetization is broken down into three main groups (of which one is an extreme case of the other). The first is ferromagnetism where all the magnetic moments align under an applied magnetic
field. The second is ferrimagnetism where the magnetization breaks into two distinct magnetic moments where one aligns to the magnetic field and the other aligns opposite to the magnetic field with the magnitude of one magnetic moment being larger than the other. Antiferromagnetism is the extreme case of ferrimagnetism where the two magnetic moments generated cancel each other out.

Figure 1.1 Diagram showing each type of magnetism and how they relate to each other.

In a ferromagnetic material the magnetic moments of the atoms can align together into domains as shown in Figure 1.2.
Figure 1.2 Schematic of magnetic domains inside a magnetic material. The spins in the domains point in the same direction but the entire material can have no net spin.

Classical physics cannot predict magnetism, thus, it is an entirely quantum phenomenon. Magnetic materials remain magnetic below a certain critical temperature, often referred to as a magnetic ordering temperature ($T_c$). Above $T_c$, thermal energy overcomes the coupling between the magnetic moments and the domains turn into randomly oriented magnetic moments. The susceptibility ($\chi$) of a magnetic material is related to $T_c$ by

$$\chi = \frac{C}{T - T_c}$$  \hspace{1cm} (1)

where $C$ is the Curie constant and $T$ is the absolute temperature (Appendix A). The susceptibility is defined as the ratio between the magnetization of the material to the applied magnetic field.

Superparamagnetic particles are single domain particles because the physical size of the particles are so small that it is are not energetically favorable to prepare multiple domains.\textsuperscript{2,3} Superparamagnetic particles have an interesting property where their
magnetic moment spontaneously flips due to thermal fluctuations (by elongating the particle one can prepare a hindrance for this flipping). The thermodynamic criterion for keeping the spin from flipping in a superparamagnetic particle is given by

$$Kv \geq k_BT$$

where $K$ is the anisotropy constant of the paramagnetic particle, $v$ is the volume of the particle, and $k_BT$ is the thermal energy with $k_B$ being the Boltzmann constant and $T$ being the absolute temperature. As the volume of the particle decreases, the anisotropy constant needs to increase to overcome the thermal energy (the way to increase the anisotropy constant is to increase the aspect ratio of the particle). If the magnetic nanoparticles satisfy the inequality in Eq. (2), then the particles are said to be superparamagnetic.

Remnant magnetization is the residual magnetic field the particles have when the magnetic field is removed (Figure 1.3). Superparamagnetic particles do not have remnant magnetization; once the magnetic field is removed the magnetic moment of particles becomes randomly oriented. Superparamagnetic particles do have a saturation magnetization that is relatively high because all the magnetic moments can align with the field. Saturation magnetization occurs when the field aligns all of the domains (or all the particles when all the particles are superparamagnetic) and is schematically shown in Figure 1.3.
Figure 1.3 Schematic of the plots of magnetization (M) versus magnetic field (H) for a magnetic material showing coercivity. When the system reaches the saturation magnetism the domain structure of the material (if multi–domains) appears as shown next to the saturation plateau.

A hallmark of multi–domain (large particles) and single domain (highly anisotropic) particles is coercivity\(^6\). If the particles are roughly spherical they will have no coercivity since the magnetic domain will be able to move more freely. If the particles are elongated, the coercivity will increase significantly (higher coercivity means the particle keeps it's magnetization under no field, which is useful for magnetic recording).\(^1,3,6,7\) If the highly anisotropic particles are still single domain but large size (near the threshold for multi–domain particles), then the particle will have the highest coercivity.\(^6\)

When spherical superparamagnetic particles are under an applied magnetic field, they do not orient “end–to–end” with each other to prepare a chain of particles. However, the multi–domain magnetic particles will orient.\(^8,15\) When put in a solvent and coated with a sufficient amount of surfactant to prevent agglomeration and settling, this chain
growth can affect the optical and rheological behavior of the suspension. It is a ferrofluid if single domain particles are suspended and as a magneto–rheological fluid if the particles are multi–domain and on the order of 1 µm. Real ferrofluids have some multi–domain particles since (as discussed later) these ferrofluids will have a particle size distribution.

The aggregation of magnetic particles affects the polarization of the incident light causing a change in the polarization through the sample. These chain aggregates also induce light scattering. Using dichroism one can also determine the orientation of aggregates. These chain aggregates also affect the rheological behavior of ferrofluids under an applied magnetic field perpendicular to the shearing direction. Under small strains the ferrofluid produces a yield stress very similar to a Bingham fluid. Using small–angle neutron scattering (SANS) researchers found that the chains move as a whole when sheared as schematically shown in Figure 1.4.

**Figure 1.4** (a) Under no shearing the chain of particles aligns along the magnetic field and (b) when the top plate moves, the side of the chain closest to the top plate moves in the direction the plate is moving (arrow in b).
CHAPTER II

LITERATURE REVIEW

2.1 Synthesis of Ferrofluid

Ferrofluids have magnetic particles on the order of 10 nm in a carrier liquid. The magnetic particles are coated with a surfactant, which allows the particles to be dispersed in the carrier liquid. Figure 2.1 shows schematically the role the surfactants play in a ferrofluid.

![Magnetic particle coated with a surfactant consisting of a polar head and non–polar tail.](image)

**Figure 2.1** Magnetic particle coated with a surfactant consisting of a polar head and non–polar tail.

The typical synthetic route to prepare magnetic particles begins with the reduction of Fe(II) and Fe(III) salts with a base. By controlling the pH of the system one can control the particle size. Once this is done, a surfactant is added (a common surfactant is...
oleic acid (with the chemical structure shown below) with a base to prepare a charge on the surface of the magnetic particle, so that the surfactant can reside at the surface of the particle. Another widely used method is high-energy ball milling. In this process large magnetic particles are ground into sub-micron sized particles. This is commonly done to produce commercial ferrofluids because the production cost is relatively low. The ground material is then coated with an appropriate surfactant but unlike the chemical synthesis they can mill the particles in the presence of the surfactant causing the magnetic particles to get entangled in the surfactant's aliphatic chain.

The quality and quantity of a surfactant residing at the surface of the magnetic particles affect the amount of energy needed to agglomerate the particles. Since magnetic particles are used to make seals, these ferrofluids must be able to retain their dispersion under high magnetic fields. But even when the particles are completely coated with a surfactant, some agglomerations can still be present.

2.2 Structure of Ferrofluids under an Applied Magnetic Field

When a magnetic field is applied to a ferrofluid the particles tend to align with the magnetic field. If the interaction is strong enough, the attractive energy of the particles (interaction energy) may overcome the energy keeping the system dispersed (it may produce aggregation).
2.2.1 Aggregation of Magnetic Particles under an Applied Magnetic Field

There are several types of structures that can form in a ferrofluid under an applied magnetic field. Using neutron scattering one can observe an ordering taking place at relatively low magnetic fields.\textsuperscript{42,43} Under higher magnetic fields the structures become visible by optical microscopy and one observes needle–like structures as shown in Figure 2.2.

![Pattern evolution of a ferrofluid film in an applied magnetic field.\textsuperscript{44}](image)

**Figure 2.2** Pattern evolution of a ferrofluid film in an applied magnetic field.\textsuperscript{44}

Horng et al.\textsuperscript{44} showed that two separated chains merge and the chains become longer under a higher magnetic field. The chains also tend to elongate when the particle concentration is increased. After the magnetic field reaches a critical strength the ferrofluid remains unchanged.\textsuperscript{44} This needle–like structure is very predominant in ferrofluids with polydisperse magnetic particles. When one obtains a nearly monodisperse ferrofluid the needle–like structure turns into uniform columns\textsuperscript{27} which can change in size relative to the magnetic field and sweep rate of the magnetic field\textsuperscript{45}.
(Figure 2.3b). These columns (as well as the needle–like structures) appear as “dots” when looked at the direction perpendicular to the magnetic field (Figure 2.3a).

**Figure 2.3** (a) A ferrofluid under magnetic field perpendicular to the film (field coming out of paper) and (b) shows the formation of column structures under parallel magnetic field for which each column appears as a dot in (a). Images taken from Horng et al.\textsuperscript{44}

The structure of ferrofluids under perpendicular magnetic fields can take interesting shapes beyond what is shown in Figure 2.3a. Under certain circumstances the “dots” in Figure 2.3 can arrange into grain boundaries where each of the columns in the fluid align relative to each other in a specific subregion.\textsuperscript{27,44} Many researchers have reported these structures forming under applied magnetic fields, but most of their experiments were done by encasing the ferrofluid in thin cells (on the order of 15 µm). With thicker cells, the needle–like structures turn into branching structures.\textsuperscript{38}

Using an optical microscope (observes Section 2.2.2) a research group\textsuperscript{46} found a light scattering phenomenon when a ferrofluid was placed into a magnetic field. They
reported a streak of scattered rays appearing perpendicular to the magnetic field. This can be a sign that many linear–chain clusters are formed along the field direction. These structures were observed in concentrated solutions (solutions of greater than 5 wt % magnetic particles). However, no chain aggregation was observed for dilute solutions. Instead, they act as individual particles interacting weakly.

2.2.2 Theoretical Models of Phase Separation in Ferrofluids

It is well known that in concentrated solutions the magnetic particles align into chains and in dilute solutions they are weakly interacting and do not form chain aggregates (observes Section 2.2.1). There are several types of models reported to describe the chain aggregation of concentrated ferrofluids. All of them employ dipole–dipole interactions to describe the alignment of the magnetic particles (each particle has a north (N) and south (S) pole and these poles tend to align along the magnetic field (H) to prepare a structure shown schematically in Figure 2.4.

![Figure 2.4](image.png) Magnetic particles aligning along the direction of magnetic field (H).
The most popular model stipulates that the agglomeration of magnetic particles arises from phase separation (a thermodynamical process creating instability of the dispersed magnetic particles). Satoh et al. used dipole–field and dipole–dipole interactions to develop a Monte Carlo simulation. Both the 2D and 3D simulations done by Satoh found chain–like aggregation in the ferrofluid. Taketomi et al. used Debye’s critical opalescence theory to establish a thermodynamical instability theory of colloidal particles dispersion for interpreting the agglomeration behavior.

Zubarev et al. also used a model involving dipole–dipole interactions (under the limit of dilute solutions this is irrelevant because the particles do not interact but instead of using a Monte Carlo simulation they use a free energy minimization. By using this approach they were able to successfully describe the shear–dependent behavior of the ferrofluid.

2.2.3 Micelle Model of Phase Separation in Ferrofluids

It was proposed by Taketomi et al. that the formation of the chainlike aggregates is not caused by individual particles aligning, but rather by the formation of micelle and aligning. This micelle model was based on the observation of a frozen ferrofluid. When a magnetic field is applied to a frozen ferrofluid, it is expected that there would be no real change in the magnetic behavior of the sample (when frozen, the particles are unable to align). There are some anomalous effects in frozen ferrofluids in that when a sample is cooled down slowly and then reheated, their magnetic behavior changes at each cycle. The micelle model was used by some research groups to explain their experimental observations. During thawing, it was postulated by Taketomi that the
difference in the observed magnetic behavior of the solution was due to the formation of micelles while the material was thawing.

The micelle model assumes that excess surfactant is present in the system beyond what is coated on the surface of particles (for most ferrofluids this assumption is reasonably valid). When a ferrofluid is cooled down, it becomes energetically favorable for the magnetic particles to align with other particles using the excess surfactant forming circular micelle as shown schematically in Figure 2.5.

![Figure 2.5](image)

**Figure 2.5** Schematic drawing of magnetic particles aligning in a micelle creating a net zero magnetic moment.

An applied magnetic field causes the micelle to elongate and under a high enough magnetic field the micelle begins to break, causing a net magnetic moment as shown in Figure 2.6. This broken micelle can then form aggregates to produce micro clusters or chainlike aggregates as shown in Figure 2.7.
Figure 2.6 Under no magnetic field the particles align in a micelle (a). When a magnetic field is applied the micelle begins to deform as shown in (b) and (c). Under high enough magnetic field the micelle breaks producing a net magnetic moment in the direction of the applied magnetic field.

Figure 2.7 Elongated micelles forming macro–clusters that form the chain–like aggregates under an applied magnetic field.
2.3 Dichroism and Birefringence of Ferrofluids

The magneto–optical effects of ferrofluids have been studied by many research groups. There are two main magneto–optical effects for ferrofluids. The first is dichroism, and the second is birefringence.

2.3.1 Dichroism of Ferrofluids

Dichroism was originally speculated to be caused by the movement of the particles in a ferrofluid under applied magnetic fields. But later it was argued that the origin of this effect arises from anisotropy of the dielectric behavior of the magnetic particles and later cluster/chain–like aggregates forming under applied magnetic fields (a detailed discussion of the mechanism of chain formation will be discussed in the birefringence section 2.3.2). The distinction between the anisotropy of the physical particle and anisotropy of the dielectric behavior is important. The aspect ratio of the magnetic particles (since most are not perfect spheres) is defined as shape anisotropy. The directional dependence of the dielectric behavior of the magnetic particles is defined as the dielectric anisotropy. Both of these combine to determine the overall anisotropy of the particle. However, for birefringence and dichroism, the dielectric anisotropy is the most important. Since the chain–like clusters are oriented in the field direction, the average dielectric polarization of the entire medium (chains plus solvent) will be different in one direction than in the other.

When a dielectric material is inside an electric field, the dielectric material prepares an internal electric field to oppose the field outside. It does this by separating the
charges inside the material to generate an electric field, a process called dielectric polarization. The opposite of dielectric polarization is called dielectric permittivity. Dielectric permittivity is defined as the resistance of a dielectric material to form an electric field. If dielectric polarization is known, the dielectric permittivity is known.

The existence of the dielectric behavior of ferrofluids has been confirmed using capacitance measurements, where a ferrofluid was placed between the anode and cathode of a capacitor. \(^{59-65}\) From this measurement, one can observe a difference in capacitance with applied magnetic field in both the magnetic field direction, and perpendicular to the magnetic field direction. This change in capacitance is related to the change in the dielectric behavior of the material in the two directions. \(^{64,65}\) One interesting result from these experiments is that for concentrated solutions (greater than 15 volume percent magnetic particles) there appears to be no chain aggregation \(^{59}\), but this was contested. \(^{61}\)

One must be able to determine the dielectric polarization of clusters as a function of the cluster length, since the clusters have a dielectric polarization which is different than individual particles and the solvent. With both clusters and individual particles, this polarization exists in one direction more prominently than the other. However, the clusters have a much stronger anisotropy than the individual particles. The magnetic particles in a ferrofluid are on the order of 10 nm and the chains are around 1 µm thick, but since these particles and chains can absorb the electric vector (at least partially) of an electromagnetic wave, one has to regard the electric field prepared by the visible light as affected by particles. So when using visible light, the permittivity (\(\varepsilon\)) (which is analogous to the dielectric polarization) appearing in Maxwell’s equations may be taken equal to the average of the permittivity of clusters, individual particles, and solvent expressed by. \(^{22}\)
When determining the permittivity of the medium, one takes into account the dielectric constant of the chain \((e_c)\), the individual particles \((e_p)\), and the solvent \((e_s)\) as a function of the magnetic field in both the applied field direction and perpendicular direction. Knowing the permittivity one can use Eq. (3) to determine the electric displacement field \((\mathbf{D})\) caused by an electric field \((\mathbf{E})\) passing through a dielectric material.

\[
\mathbf{D} = e\mathbf{E} = (e_c + e_s + e_p)\mathbf{E}
\]  

(3)

The polarization of the magnetic particles and clusters causes an absorption of the polarized light through the sample and is thus the basis for the dichroism of the ferrofluid. The electric field absorbed by the magnetic particles and clusters/chains is defined as \(\sigma_c\). This is called dielectric polarization and is one of the predominate sources of absorption in a ferrofluid. Another type of absorption (or more specifically scattering) that must also be considered is called Rayleigh scattering. Rayleigh scattering is the elastic scattering of light from particles that are smaller than the wavelength of that light. The Rayleigh regime is defined when \(2\pi r/\lambda \ll 1\) and (where \(r\) is the radius of the particle, \(\lambda\) is the wavelength of the incident light). This scattering we will simply call \(\sigma_R\). Using the Beer–Lambert equation in terms of \(\sigma_c\) and \(\sigma_R\) one can obtain the transmissivity \(T_r\) (where the transmissivity is defined as the intensity of the light through the material divided by the intensity of the light in open air) of light passing through a magnetic fluid of thickness \(d\) as:

\[
T_r = \exp[-d \sum_{k=1}^{\infty} \nu_k (\sigma_R + \sigma_c)]
\]  

(4)
where \( v_k \) is the volume of the particles, and particle clusters/chains. Since the chains can be only several particles in size, their size may be smaller than the wavelength of light so Rayleigh scattering of the chains must be considered.

Several authors have tried to derive equations for \( \sigma_c \). The Rayleigh scattering \( (\sigma_R) \) can be easily determined. There are several approaches to deriving the chain aggregate component \( (\sigma_c) \) of the absorption shown in Eq. (4). Most researchers relate the absorption to the dielectric polarization of the chain aggregate. Several of the theories use a log normal distribution to describe the particle size distribution of the magnetic particles.

\[
f(d) = \frac{1}{\sqrt{2\pi s^d}} \exp \left[ -\frac{\ln(d-d_o)^2}{2s^2} \right]
\]  

(5)

In Eq. (5) \( d \) is the diameter of the particles, \( s \) is the standard deviation, and \( d_o \) is the mean diameter. Transmission electron microscopy (TEM) was used to determine the particle size distribution of a ferrofluid by setting up a histogram of the particle sizes. It was found that a log normal distribution fit the data very nicely to give the average particle size and the standard deviation.

Other theories just assume that chain aggregates form and thus treat the linear aggregates as a rigid rod with a distribution of dielectric anisotropies. All of these theories are used to fit the data obtained to some generalized equation that uses the Rayleigh and chain aggregate absorption. The absorption constant used for this research is defined as.

\[
I = I_o \exp[-2h_i(\mathcal{H})] \quad i = 1,2
\]  

(6)
In Eq. (6) $h_i(H)$ is a generalized absorption constant, $I_o$ light intensity at zero magnetic field, and $I$ is the intensity of the light at a given magnetic field. In Eq. (6), 1 and 2 denote the ordinary and extraordinary rays, respectively. Referring to Figure 2.8, the extraordinary ray is when $\beta$ is set to 90 degrees and the ordinary ray is when $\beta$ is set to 0 degrees. The derivation of Eq. (6) is given in Appendix B. The dichroism experiment is setup by having the analyzer removed from the optical setup (Figure 2.8) and having the angle $\beta$ be set at 0 degrees along the y axis and 90 degrees along the z axis.

Figure 2.8 Schematic of the birefringence experiment along with the coordinate system used for the theory to determine the birefringence.\textsuperscript{56}

Using the configuration given in Figure 2.8 (removing the analyzer) Taketomi et al. were able to determine the normalized transmissivity (defined as the ratio between the light output from the sample under an applied magnetic field to the light output with no
magnetic field applied). Figure 2.9 gives the data for two different ferrofluids with
different surfactant layers.\textsuperscript{72}

\textbf{Figure 2.9}. (a) Normalized transmissivity versus magnetic field for oil–based ferrofluid with thick surfactant coating at volume \% concentrations of 0.023 (□), 0.046 (○), 0.070 (△), and 0.093 (▽); (b) for an oil–based ferrofluid with a thin surfactant coating at volume \% concentrations of 0.023 (□), and 0.046 (○). The filled and unfilled points correspond to the ordinary and extraordinary ray (respectively).\textsuperscript{71}

One can observe from Figure 2.9a that when the magnetic field increases the ordinary ray’s (defined as the ray when the polarizer is set to β = 0) intensity increases while the extraordinary ray’s intensity decreases. For the extraordinary ray, the intensity decreases because the particles are aligning in the direction of the extraordinary rays. This causes the electric field to polarize the particles (due to the particles absorbing part of the electric field component of the transmitted light) decreasing the intensity of the light. Since the particles are orienting parallel to the magnetic field, the extraordinary ray (which has its electric field perpendicular to the chain aggregation) observes an increase in intensity since it now has less particles aligned perpendicular to the magnetic field.\textsuperscript{22,71}

Figure 2.9b shows a different trend. As the magnetic field increases both the ordinary and
extraordinary ray’s light intensity decreases. According to Socoliuc\textsuperscript{71,72} this was attributed to Rayleigh scattering being the more predominant mechanism for the change in the light intensity. Soculiuc concluded that chain aggregation is not the most prominent mechanism in this ferrofluid used. It is still unclear how Rayleigh scattering can decrease the light intensity as a function of the magnetic field in both the ordinary and extraordinary rays.

2.3.2 Birefringence and Particle Agglomeration in Ferrofluids

Birefringence in ferrofluids was first observed by Majorana.\textsuperscript{73} He found a birefringence in dilute magnetic colloidal solutions. Many authors afterwards have found similar phenomena.\textsuperscript{13-15,74,75} These studies, however, focused on dilute magnetic fluids because magnetic fluids even at lower concentrations (one \% by volume) are opaque, so solutions less than one volume percent were used. Other researchers used thin film samples of higher concentration ferrofluids (1–20 \% by volume) where the thin films were around 10 \( \mu \)m thick.\textsuperscript{56}

Initial work involving birefringence assumed the orientation of permanent magnetic moments along the magnetic field. This gave rise to the change in refractive index.\textsuperscript{76} Later it was found that another mechanism besides magnetic moment alignment was taking place since for moderately concentrated ferrofluids the Langevin equation no longer experimentally fit the data. The following expression is sometimes used for fitting the experimental light intensity to the Langevin function:\textsuperscript{77}

\[ I = I_0 f(y)L(mH/K_B T) = I_0 f(y)(\coth(mH/k_B T) - 1/(mH/k_B T)) \quad (7) \]
where $L(mH/k_BT)$ is the Langevin function, $f(y)$ is a distribution function, and $M_S$ is the saturation magnetization, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. Equation (7) is valid only in dilute solution since the derivation for the Langevin function assumes non-interacting single domain particles. Some research groups\cite{77} have tried, with minimal success, to modify Eq. (7) by adding dipole–dipole interactions. By assuming the log normal distribution of particles as the distribution function $f(y)$, researchers have found relatively good agreement in the dilute regime.\cite{74}

For most ferrofluids, the assumptions of the Langevin function are violated (even in dilute solution there are some particles that are multidomain due to there being a distribution of particles). The large multidomain particles interact under relatively low concentration forming tail–to–head giving rise to chain aggregate formation.

Now it is known by use of TEM\cite{78,79} and optical microscopy\cite{8-10,14,18,19,26,27,40,44,80-82} that chain formation occurs in ferrofluids that have a small amount of ferromagnetic particles (Figure 2.10).
Figure 2.10 Transmission electron microscopy image of magnetic particle of 6.9 nm and iron volume percent 0.06 and for (b) 0.06 iron volume percent of 6.9 nm and 0.04 iron volume percent of 2.1 nm particles. (a) is under no magnetic field while (b) has a magnetic field of 1.6 Tesla applied.78

Figure 2.10 shows that even with low particle concentration, multidomain magnetic particles align under no magnetic field (Figure 2.10a) due to dipole–dipole interactions. Under saturation magnetic field the particles form chain structures (Figure 2.10b) due to the attractive dipole–dipole interactions between the particles. Since these are iron particles and not iron oxide particles, they can be ferromagnetic at smaller particle sizes than iron oxide particles (iron oxide particles have an oxide coating that is nonmagnetic, so iron oxide particles need to be larger to have the same magnetic moment as iron particles).78 The reason for this is that the iron oxide particles have an oxide layer that does not add to the magnetic behavior.
The research done in ferrofluids focuses on how to theoretically determine the
birefringence, dichroism, and agglomeration of magnetic particles. Most of the models
used to describe the birefringence of ferrofluids assume that the absorption of the light is
related to the dielectric anisotropy of the magnetic particles in the magnetic fluid. The
theories dealing with the birefringence of ferrofluids are continuations of the theories for
dichroism. The main differences between the theories for birefringence are how they
define the dielectric anisotropy (identical to the differences in the theories explaining
dichroism). For dilute solutions, one uses the Langevin parameter considering only non–
interacting single domain particles (Eq. (7)), from these one can determine the particle
size. The remaining models dealing with concentrated ferrofluids can be broken
down into two main groups. The first assumes that the chain formation takes place and
derives a theory to relate the dielectric anisotropy of the defined chains to the absorption
of the light. The second group of theories deals with the agglomeration of
the magnetic particles and then derives the theory to relate the dielectric
anisotropy of the agglomeration to the absorption of light. All of these theories assume
linear chain structures which is not necessarily true since branching structures and other
three dimensional structures can form.

In the agglomeration theories all of the researchers define the dipole–dipole
interaction of the particles as some variation of the following equation. In Eq. (8) U is the interaction energy between two dipoles ($\vec{\mu}_1$ and $\vec{\mu}_2$), r is the distance
between the two dipoles, and $\mu_\circ$ is the permittivity of free space. When the two dipoles

\[ U = \frac{\mu_\circ}{4\pi} \left[ \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{R})(\vec{\mu}_2 \cdot \vec{R})}{r^5} \right] \tag{8} \]
are pointing in the same direction and equal (in the case of no particle size distribution and high magnetic field) Eq. (8) reduces to:

$$U_{\text{max}} = -2 \frac{\mu_0}{4\pi} \left( \frac{\mu^2}{\nu^3} \right)$$  \hspace{1cm} (9)$$

where $\mu = (4/3)\pi a_m^3 m_s$ with $a_m$ being the particle radius and $m_s$ being the magnetic moment of the particle. It is worth noting that $U_{\text{max}}$ is proportional to $a_m^6$ which means that as the particle size increases, the magnetic interaction increases by the sixth power. It is also worth noting that, as the distance between the particles increases, the interaction energy decreases. This explains why dilute solutions can still form some chain aggregation under high magnetic fields.

The agglomeration theories have some trends in common. At high dipole–dipole interaction, the magnetic particles combine to form short flexible chains even under no magnetic field as observed in Figure 2.10a. These chains increase in length with magnetic field and particle concentration. These theories do, however, only take into account monodisperse ferrofluids. With polydisperse ferrofluids researchers found (through simulations) that the smaller particles do not have as strong an effect on the chain formation as the larger particles (the surfactant repulsion forces can overcome the attractive forces of the magnetic particles). This gave rise to the generally accepted theory that single domain particles do not contribute to the chain formation. However, it was found that they do take part in the chain growth once the chain is already formed by the larger particles.\textsuperscript{90}
2.3.3 Birefringence Experiment

There are two main experiments for birefringence. The experimental setup used in this article is shown schematically in Figure 2.8. The second type of experiment used to determine the birefringence of a ferrofluid is called the null ellipsometry method and is shown in Figure 2.11. The null ellipsometry setup depicted in Figure 2.11 was not used due to problems with magnetic field strength.

![Figure 2.11 Schematic of the null ellipsometer experiment where P is the polarizer, Q is the quarter wave plate, and A is the analyzer.](image)

For the experimental setup in Figure 2.8, some researchers used a compensator between the sample and the analyzer and determined the phase difference. Others used the exact setup in Figure 2.8 and determined the retardation ($\delta$) by using the following formula:

$$\sin \delta = 2\sqrt{I_{\text{min}}/I_{\text{max}}} \cosh (h_2 - h_1)/(1 + I_{\text{min}}/I_{\text{max}})$$  \hspace{1cm} (10)

where $I_{\text{min}}/I_{\text{max}}$ is the intensity of the light output when the polarizer and analyzer are crossed ($I_{\text{min}}$) and not crossed ($I_{\text{max}}$). The absorption constants ($h_1$ and $h_2$) are given in
Eq. (6). By solving Eq. (10) for $\delta$ one can determine the birefringence ($\Delta n$) with the following relation:

$$\delta = 2\pi \Delta n \frac{d}{\lambda}$$

(11)

where $d$ is the thickness of the sample and $\lambda$ is the wavelength of the laser light used.

The derivation of Eq. (10) is given in Appendix A.

A typical phase difference versus magnetic field curve is shown in Figure 2.12 where one notes that as the magnetic field increases the phase difference ($\delta$ in Eq. (11)) increases.

![Figure 2.12](image)

**Figure 2.12** Phase difference versus magnetic field for a double surfactant, water–based magnetic fluid. Inset is the reduced magnetization (ratio of the magnetization over the saturation magnetization) of the magnetic fluid used determined by magnetometer measurements.

Some researchers have dealt with the particle size distribution and how it affects the birefringence of ferrofluids. Patel et al. have shown that as the concentration of
magnetic particles decreases, so does the retardation. Still others have shown that the quality of surfactant (the surfactant layer thickness) affects the chain formation mechanism.\textsuperscript{71} To date, only one research group has investigated how excess surfactant affected the optical behavior of ferrofluids. Rousan et al.\textsuperscript{99} measured the transmission of light from a ferrofluid cell with different concentrations of surfactant. As the surfactant concentration increases, the transmission coefficient increases. This experiment is schematically shown in Figure 2.8. However, instead of the magnetic field being applied in the z–direction, it is applied in the x–direction. Figure 2.13 shows plots of transmission coefficient (R) defined by:

\[ R = I/I_o \]  \hspace{1cm} (12)

versus magnetic field. In Eq. (12) I is the incoming light to the analyzer under an applied magnetic field and \( I_o \) is the incoming light to the analyzer under zero magnetic field.

\textbf{Figure 2.13} Plots of transmission coefficient (R defined in Eq. (12)) versus magnetic field (KA/m) with surfactant concentration.\textsuperscript{99}
Figure 2.13 shows that as the surfactant concentration increases the transmission coefficient decreases. Rousan\(^9\) claimed that this was due to the surfactant hindering the chain aggregation process. The structure formed under the experiment done by Rousan is shown in Figure 4.14 where the image is taken in the direction of the applied magnetic field for a ferrofluid with low surfactant concentration.

**Figure 2.14** Micrographs of magnetic particle columns in a ferrofluid with an applied magnetic field going through the page and each column is roughly 1 micron in size.\(^8\)

Figure 2.14 shows that as the magnetic field increases, so does the number of “dots”, where the dots are actually columns of magnetic particles (the average particle size is 10 nm and these columns are roughly 1 micron in thickness). By looking at Figures 2.14 and 2.13, one should note that Rousan’s data shows that the transmission of light should increase with applied magnetic field. Data presented by several authors
shows that as the magnetic field increases, the absorption of light increases (but this is for magnetic fields perpendicular to the incident light).\textsuperscript{22,24,55,100}

It is unclear from reading the paper by Rousan what the concentration of the surfactant was, at what magnetic particle concentration the solution was, and exactly what the concentration of surfactant was in comparison to that of the magnetic particles. It was also not explicitly mentioned whether the added surfactant was bonded to the particles (if they were added after or during the ferrofluid was made).

The temperature dependence\textsuperscript{24,26,77} of the birefringence is of practical concern. If chain formation was the sole reason for birefringence, then one would observes the birefringence decreasing as a function of temperature. The reason for this is that the thermal energy adds kinetic energy to the particles. This added kinetic energy to the particles could prevent the particles from staying in the chains. As discussed earlier (Section 2.2.2) the single–domain particles aligning along the magnetic field (either the physical particles or the dielectric anisotropy) causes dichroism and thus birefringence. These single–domain particles (that do not form chain aggregates) would have more thermal energy to move (due to the increased temperature) under applied magnetic field. One would also observe a ferrofluid consisting of only single–domain particles to decrease its birefringence as the temperature increases. As the temperature increases, the birefringence increases up to a critical value where it begins to decrease\textsuperscript{77} (Figure 2.15).
The results of the experiments taking into account the temperature dependence of ferrofluids find that at higher temperatures, the kinetic energy of the particles can be greater than the energy trying to bind the particles into a chain. Other researchers have also found the increase in distance between particle chains as the temperature increases.

The birefringence of a magnetic fluid has a great dependence on thickness. As the thickness of the fluid film decreases, the magnetic particle aggregation is hindered due to restrictions in motion and in three dimensional structures. To date, there is not much data comparing the variation of birefringence with film thickness.

The frequency of the magnetic field applied also affects the birefringence of magnetic fluids. Several researchers noticed that this effect contributes to two different types of relaxation that are in ferrofluids. Even though chain aggregation contributes to
the birefringence of ferrofluids the alignment of the magnetic particles also contribute. There are two types of rotation of the magnetic particles. The first is Brownian rotation where the magnetic moment is frozen in the particle (a ferromagnetic particle) and thus the entire particle must rotate to align its magnetic moment to the magnetic field (small particles that are highly anisotropic also have to do with this). The second mechanism is Neel relaxation\textsuperscript{13} where the magnetic moment can be rotated to align with the magnetic field without the particles needing to rotate. The energy barriers for both of these mechanisms are anisotropy energies. Neel relaxation and Brownian relaxation take place in a ferrofluid, but the one with the shorter relaxation time dominates. Brownian rotation is assumed to be the cause of chain aggregates, since this requires the particles to physically move while Neel relaxation is assumed for particles that are single domain (and as such do not form chains). The frequency of the magnetic field can be used to determine which one of these is dominant. This frequency dependence is of immense importance in the field of hyperthermia\textsuperscript{102-104} where one oscillates the magnetic field and needs particles that have their relaxation at the same period of the oscillation to produce the maximum amount of movement and thus the highest temperature gain (the movement causes heat generation). Relaxation is one of the predominant factors in discussing the rheological behavior of ferrofluids.

2.4 The Rheological Behavior of Magnetic Fluids

The rheological research conducted on magnetic fluids has focused primarily on the concentration of the magnetic fluid, particle size (or particle size distribution), and relaxation process. The following section will be broken down into three parts; the rheology of dilute/concentrated ferrofluids, the effect of particle size distribution on the
rheological behavior, and the relaxation process in ferrofluids. Then we will present a brief review of the current theories used to theoretically determine the rheological behavior of ferrofluids.

2.4.1 Dilute Ferrofluids

Using a dilute solution of cobalt particles, McTague\textsuperscript{105} found that the viscosity of the suspension increased as the applied magnetic field increased. Several other research groups have reported this trend as well for a variety of ferrofluids.\textsuperscript{29,44,106-111} Typical, normalized plots of viscosity versus magnetic field strength are given in Figure 2.16. Most of the rheological measurements (especially viscosity) are done in a capillary rheometer where the magnetic field is applied perpendicular to the flow of the liquid. For yield stress, a cone–plate rheometer was utilized\textsuperscript{112-114} for steady–state shear flow. A parallel–plate rheometer was also used for viscosity measurements interchangeably with a cone–plate rheometer (with the exception that for yield stress a cone–plate rheometer was used only). To date no one has investigated the difference in rheological behavior measured by both cone–plate and a plate–plate rheometer.
It is observed in Figure 2.16 that the viscosity decreases as the shear rate increases (shear-thinning). This phenomenon was not explained in the work by Shliomis and Rosensweig, but later the theories by Zubarev were able to explain this shear-thinning behavior.

Shliomis\textsuperscript{92} derived equations for the magnetic field dependence of the viscosity which works well for dilute ferrofluids (where the particles are unable to interact) but does not work well in concentrated solutions or solutions with magnetic particles greater than 15 nm.\textsuperscript{31,92,115} The equation derived from Shliomis is:

\[
\eta_{r(H)} = \frac{3}{2} \eta_0 \varphi' \frac{a-\tanh a}{a}\langle \sin^2 \beta \rangle 
\]

where \(a = \mu_0 m H / k_B T\), and \(\varphi'\) is the volume fraction of the magnetic particles including the surfactant coating, \(\beta\) is the angle between magnetic field direction and vorticity of the flow, \(\langle \cdots \rangle\) denotes a spatial averaging, \(m\) is the magnetic moment of the particle, \(k_B\) is
Boltzmann’s constant, and $T$ is the absolute temperature. Equation (13) takes into account the vorticity of non–interacting particles to determine the viscosity change under an applied magnetic field of a ferrofluid. The vorticity of the particle is the rotation of the particle resulting from the velocity of the fluid.

The theories introduced by Rosensweig, and subsequently improved on or rederived by others, to understand viscosity change as a function of magnetic field is called ferrohydrodynamics.\textsuperscript{116-118} Ferrohydrodynamics has had great success in guiding the development of practical applications in ferrofluids like rotational shaft seals\textsuperscript{88,119,120} and voice coils.\textsuperscript{121} The theory by Shliomis takes into account Brownian motion of the small magnetic particles where the theory by Rosensweig does not take this into consideration. The theories by Shliomis and Rosensweig are limited to dilute ferrofluids (magnetic particle concentration less than 0.1% by volume) because it assumes no particle–particle interactions.

### 2.4.2 Concentrated Ferrofluids

Rosensweig\textsuperscript{122} observed the change in viscosity for a concentrated magnetic fluid consisting of mostly superparamagnetic particles (the mean diameter of 10 nm determined by SEM images of 250 particles). Concentrated ferrofluids increase particle–particle interactions, and this gives rise to increased chain aggregation and results in a yield stress (if the ferrofluid has some magnetic particles greater than 15 nm). The theories of Rosensweig and Shliomis do not, however, explain yield stress that is commonly observed in ferrofluids with small amounts of particles larger than 15 nm.\textsuperscript{11,30,32,35,123-126} Figure 2.17 shows the yield behavior of a ferrofluid under different
applied magnetic fields. The fluid used in Figure 2.17 is a concentrated (17% by volume) ferrofluid.

![Figure 2.17 Plot of the shear stress versus shear rate for a ferrofluid under 500 (♦), 400 (○), 300 (●), 200 (□), 100 (★), and 50 (△) Oe.](image)

**Figure 2.17** Plot of the shear stress versus shear rate for a ferrofluid under 500 (♦), 400 (○), 300 (●), 200 (□), 100 (★), and 50 (△) Oe.\(^{127}\)

In these ferrofluids, chain aggregates cause a yield stress that was not observed by Shliomis due to the particles in their work only being single domain (and low concentration). The yield phenomenon has been described by a Bingham model.\(^{128-131}\) This yield phenomenon (called the magnetorheological effect) is present in ferrofluids with some large particles but is more pronounced in magnetorheological fluids. This effect was also found in inverse ferrofluids\(^{36,130,132,133}\) where micron–sized non–magnetic particles were dispersed in a ferrofluid carrier (the rheological behavior of even inverse ferrofluids were weaker than magneto–rheological fluids, but stronger than superparamagnetic ferrofluids). Inverse ferrofluids were generally used to test computational or theoretical models since non–magnetic particles like silica or latex can
be synthesized with more control (narrower particle size distribution) than ferromagnetic particles.\textsuperscript{129,130,134}

Chain aggregation also explains the occurrence of shear thinning at higher shear rates. The work of Zubarev\textsuperscript{11,35,110,125,135} found that chain aggregates explain the dramatic increase in viscosity in an applied magnetic field. To understand the magnetoviscous effect for ferrofluids one needs to take into account the superparamagnetic particles that do not interact (Shliomis' theory) and the interacting particles (Zubarev) in order to completely determine the magnetoviscous effects for ferrofluids under an applied magnetic field. Shear thinning is also observed which can be explained by the chain aggregates breaking up at higher shear rates.

For magnetorheological fluids (and to a lesser extent ferrofluids) one observes a Weissenberg effect\textsuperscript{136,137} where the ferrofluid/magnetorheological fluid creeps up a rotating shaft under an applied magnetic field. For ferro fluids this has to be done under microgravity conditions since the effect is very small. The Weissenberg effect in polymers is due to the entangled polymer chains climbing up the shaft (instead of centrifugal force pushing the chains away from the shaft) due to the first normal stress difference being much larger than the shear stress. For ferrofluids having large enough particles to induce chain aggregates this explanation also works (but the effect is much weaker since these chains break easily).

Since magnetorheological fluids have much larger particles this effect is easily observed, but these particles also sediment out quickly. Figure 2.18 shows the height of the meniscus of a ferrofluid surrounding a rotating shaft as a function of magnetic field.
Figure 2.18 Plot of the height of the meniscus of a ferrofluid under constant rotation as a function of magnetic field.\textsuperscript{137}

To date this is the only experiment confirming viscoelastic behavior of ferrofluids. Viscoelastic relaxation,\textsuperscript{112,138,139} which is much larger than that predicted by ferrohydrodynamical theories,\textsuperscript{92,115,117,118} is also partially explained by using the theories of Zubarev.\textsuperscript{11} The calculated relaxation times using these models are one to two orders of magnitude less than experimentally observed relaxation times.\textsuperscript{135,140} These theories help explain the Weissenberg effect and to date not much research has been done on the viscoelastic relaxation of ferrofluids since this is fairly weak (the Weissenberg effect for ferrofluids has to be done under microgravity conditions). Using the theory of Zubarev\textsuperscript{140} and Batchelor\textsuperscript{141} one can also calculate the average stress tensor that agrees with experimental results if the magnetic particle concentration is less than 16\%.\textsuperscript{142} A modification of Shliomis’ theory\textsuperscript{93} shows negative viscosity which was experimentally determined earlier by Shliomis.\textsuperscript{143} Negative viscosity is defined as the...
viscosity drop, relative to the zero magnetic field viscosity, caused by an oscillating magnetic field. When a constant magnetic field is applied to a ferrofluid the viscosity increases due to the resistance of flow prepared by oriented magnetic particles impeding the free rotation of the magnetic particles. In oscillating magnetic fields (at certain frequencies) the vorticity favors rotation (where the magnetic energy is partially transformed into angular momentum of the particles). This is then converted into a hydrodynamic motion of the fluid causing the viscosity to decrease.

In his experiment Shliomis\textsuperscript{143} used Co–Ferrite particles that were highly anisotropic (high aspect ratio) so that even though the particles were small (roughly 10 nm) they maintained their magnetic moment even under high magnetic fields. The magnetic fluid was under Poiseuille flow in a capillary tube (d = 1 mm). The magnetic field direction in the capillary was parallel to the flow. When using a 20 volume percent ferrofluid in water and setting the magnetic field to oscillate he observed a change in apparent viscosity which might have prepared a negative apparent viscosity. Figure 2.19 shows the apparent viscosity verse magnetic field under various frequencies.\textsuperscript{93,143}
2.4.3 Effect of Particle Size on Rheological Behaviors of Ferrofluids

Odenbach\textsuperscript{123,144} was able to determine that small portions of larger particles cause chain aggregates (Figure 2.20), which is the main factor in describing both the yield phenomenon, and the increase in viscosity observed beyond what the model by Shliomis can predict. Figure 2.21 shows the results for ferrofluids of different particle size distributions. By looking at Figure 2.21 one can observe several important characteristics. The first is the viscosity change as the shear rate increases (explained by breakage of the chain aggregations). One can also observe that as the average particle size decreases the viscosity change decreases (particle sizes are given in the caption of Figure 2.21).
Figure 2.20 Schematic of the effect a parallel–plate rheometer (with shearing ($\gamma$) due to the top plate) has on the chain aggregates in a ferrofluid.\textsuperscript{145}

Figure 2.21 Viscosity change versus magnetic field for 5 different average particle sizes: F1 = 8.3 nm; F2 = 8.8 nm; F3 = 9.2 nm; F4 = 9.2 nm; and F5 = 10.1 nm at different shear rates.\textsuperscript{113}
One should also consider how the yield stress is affected by particle size. Table 1 gives the yield stress as a function of particle size.

**Table 1** Yield stress for APG513A ferrofluid and F2–F5 which has the particle size distribution shown in Figure 2.21 for three different magnetic field strengths.\(^\text{146}\)

<table>
<thead>
<tr>
<th>Fluid</th>
<th>(\sigma_y (B=10^3 A/m)) (\times 10^4 N/m^2)</th>
<th>(\sigma_y (B=20^3 A/m)) (\times 10^4 N/m^2)</th>
<th>(\sigma_y (B=30^3 A/m)) (\times 10^4 N/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APG513A</td>
<td>0.23</td>
<td>1.05</td>
<td>3.6</td>
</tr>
<tr>
<td>F5</td>
<td>1</td>
<td>1.07</td>
<td>11.8</td>
</tr>
<tr>
<td>F4</td>
<td>0.5</td>
<td>2.08</td>
<td>6.2</td>
</tr>
<tr>
<td>F3</td>
<td>0.46</td>
<td>1.15</td>
<td>3.8</td>
</tr>
<tr>
<td>F2</td>
<td>0.12</td>
<td>0.25</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 1 shows that as the average size of the particles increases (F2 is the smallest particle size and F5 is the largest) the yield stress also increases. One also observes that as the magnetic field increases the yielding behavior increases.

To our knowledge no one yet conducted a study on the effects of surfactant on the chain formation and rheology of ferrofluids. The study of Rosensweig\(^\text{117}\) shows a thermodynamic stability criterion for the synthesis of stable magnetic nanoparticles (stabilized by gravitational, van der Waals attraction, and dipole–dipole attraction).
3.1 Characterization of Ferrofluids

A series of ferrofluids were purchased from Ferrotec. To understand the optical and rheological behavior of these ferrofluids, the particle size, particle size distribution, surfactant concentration, particle concentration, and type of surfactant were determined. The surfactant concentration and particle concentration were provided by Ferrotec, and the types of surfactant were determined by infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The particle size and particle size distribution were determined using X–ray diffraction (XRD), and transmission electron microscope (TEM).

3.2 Preparation of Thin Ferrofluid Films.

To prepare thin film samples (between 5–100 µm) for the static birefringence and dichroism experiments, two glass slides were used. The ferrofluid was sandwiched between the two glass slides as shown schematically in Figure 3.1a. Epoxy resin was applied to seal the cell from the atmosphere. For thicker samples, Mylar sheets of a known thickness were cut and sandwiched between the two pieces of glass as shown schematically in Figure 3.1b.
Figure 3.1 Sample preparation for producing thin ferrofluid films; (a) a glass cover on top of the glass slide was sandwiched with a ferrofluid between the two glass plates; (b) Mylar sheets of known thickness were cut and sandwiched between two glass plates.

3.3 Experimental Methods

TEM images of the ferrofluids were taken at room temperature. The ferrofluid was diluted and a drop was evaporated onto the copper mesh substrate. A transmission electron microscope (JEM1200EX 11, JEOL) operated at 120kV was used to obtain the images of the magnetic nanoparticles. Ten random pictures were taken of each ferrofluid sample. Using ImageJ software the particle sizes were put into a histogram. This histogram was fitted with the log–normal distribution to determine the average particle size and standard deviation.

A Physica MCR 301 cone–and–plate Magneto–Rheometer (Anton Paar) was used to measure the transient and steady–state shear flow behavior of the chosen ferrofluids. This system was equipped with a 1 Tesla magnet, applying a magnetic field perpendicular to the shear direction. A cone–and–plate fixture was used to measure the
transient shear flow of the magnetic fluids along with a parallel–plate fixture. The results of these two measurements were compared.

The chainlike structures of a ferrofluid sample were photographed using a Leitz Laborlux 12 Pol S polarized optical microscope equipped with a hot stage (Instec) and a digital camera (Spot insight 2, Diagnostic Instrument Inc.). Thin ferrofluid films prepared for the birefringence and dichroism experiment were used to conduct the POM experiment.

X–ray diffraction was used to determine the particle size from powder samples of each fluid. The samples were dried and then ground with a mortar and pestle until they became a fine powder. The powder was then dusted on amorphous tape and from the line width and the Scherrer formula below, the average particle size was determined.

$$d = \frac{k\lambda}{\beta \cos(\theta)}$$  \hspace{1cm} (14)

where \(d\) is the diameter of a particle, \(k\) is the anisotropy constant (which for spherical particles \(k = 0.9\)), \(\lambda\) is the wavelength of the X–rays, \(\beta\) is the full–width–half–maximum of the peak (after correcting for line broadening due to instrument uncertainty) and \(\theta\) is the Bragg angle. The line broadening is the uncertainty (in degrees) that the diffractometer has. This was not corrected due to a lack of a standard sample but it would be corrected by subtracting the full–width–half–maximum of the peak by the broadening to give \(\beta\).

Infrared (IR) spectroscopy was implemented to determine the differences in the surfactant between each sample. One should observe no differences since all the surfactants used in the experiments performed should be identical.

\(^1\)H NMR spectra were obtained using a 300 MHz Varian Gemini–300 spectrometer. The surfactant type was determined using this technique where the
magnetic particles were separated from the fluid using a 7000 Oe permanent magnet. Deuterated chloroform (CDCl$_3$–$d$) was used as a solvent.

3.4 Steady–State Birefringence Measurements of Ferrofluids under an Applied Magnetic Field.

An instrument to measure the birefringence of a thin ferrofluid film under an applied magnetic field was constructed, similar to that reported in the literature.$^{22,44,56}$ A series of birefringence experiments of thin ferrofluid films were conducted.

3.4.1 Construction of a Magneto–Optical Apparatus.

For this study a magneto–optical apparatus was constructed. A schematic of the apparatus is shown in Figure 2.8 in Chapter II. Below is the theoretical background which enabled us to determine static birefringence of ferrofluids.

3.4.2 Measurements of Steady–State Birefringence of Ferrofluids.

According to Taketomi$^{21}$, the birefringence ($\Delta n$) of a ferrofluid may be determined from

$$\Delta n = \varphi \frac{\lambda}{2\pi d} \quad (15)$$

in which $\lambda$ is the wavelength of the light in vacuum, $d$ is the thickness of the ferrofluid film, and $\varphi$ is the phase difference between the two beams, one whose electric field vector is perpendicular to the magnetic field applied to the ferrofluid and the other whose electric field vector is parallel to the magnetic field. Referring to Figure 2.8 the retardation can be determined from the following expression$^{20,22,56}$

$$\sin \delta = 2\sqrt{l_{\min}/l_{\max}} \cosh (h_2 - h_1)/(1 + l_{\min}/l_{\max}) \quad (16)$$
in which $I_{\text{max}}$ denotes the maximum intensity of transmitted light (at $\theta = 0$ which is in the y axis) and $I_{\text{min}}$ denotes the minimum intensity of the transmitted light (at $\theta = \pi / 2$ which is in the z axis) while the polarization plane of the analyzer plate is rotated (observes Figure 2.8). Further, $h_1(H)$ and $h_2(H)$ appearing in Eq. (16) denote the absorption coefficients which can be determined from the following expression\(^{147}\)

$$I(H) = I_{0i}\exp[-2h_i(H)], \quad i = 1, 2$$ (17)

in which $I(H)$ is the intensity of the beam passing through the thin magnetic film in the presence of magnetic field $H$, $I_{0i}$ is the intensity of the beam passing through the thin magnetic film in the absence of magnetic field ($H = 0$), $h_1(H)$ denotes the absorption coefficient when the direction of the electric vector of the incident beam is perpendicular ($\beta = 0$) to the magnetic field and $h_2(H)$ denotes the absorption coefficient when the direction of the electric vector of the incident beam is parallel ($\beta = \pi/2$) to the magnetic field.

The following experimental procedures were employed to obtain information on static birefringence of ferrofluids. Below we will refer to the theoretical background described above, together with Figure 2.8, for the determination of birefringence of ferrofluids. (1) We inserted the thin magnetic film, removed the analyzer, and then set the polarizer at an angle of $\beta$ equal to 0 degrees and $\beta$ equal to 90 degrees (Figure 2.8), respectively, first without a magnetic field to measure the intensity of the beam passing through the sample, which enabled us to determine $I_{01}$ for $\beta$ equal to 0 degrees, and $I_{02}$ for $\beta$ equal to 90 degrees. (2) We repeated the same experiment with a magnetic field ($H$) to measure the intensity $I(H)$ of the beam passing through the thin magnetic film,
which enabled us to determine the absorption coefficient $h_1(H)$ at $\beta$ equal to 0 degrees and $h_2(H)$ at $\beta$ equal to 90 degrees using Eq. (17). (3) We inserted the analyzer into the apparatus and then measured $I_{\text{min}}(H)$ by crossing the analyzer with the polarizer which was set at $\beta$ equal to 45 degrees and determined $I_{\text{max}}(H)$ by setting the analyzer at an angle of $\theta$ equal to 90 degrees from $\beta$ (observe Figure 2.8 for the definition of the angle $\theta$). (4) Steps 2 and 3 were repeated for each applied magnetic field $H$. (5) We determined values of the phase difference $\phi$ using Eq. (16). (6) Finally, we determined the birefringence $\Delta n$ using Eq. (15).
CHAPTER IV
CHARACTERIZATION OF MAGNETIC FLUIDS

4.1 Introduction

Table 2 shows the volume percent concentration of magnetic particles, surfactant, and carrier liquid for the ferrofluids employed in this study.

Table 2 Ferrofluids employed along with nanoparticle, surfactant, and carrier fluid concentrations (all concentrations in vol. %).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Nanoparticle (%)</th>
<th>Surfactant (%)</th>
<th>Carrier Fluid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMG 900</td>
<td>17.7</td>
<td>15</td>
<td>67.3</td>
</tr>
<tr>
<td>EMG 900–I</td>
<td>15.39</td>
<td>26.08</td>
<td>58.52</td>
</tr>
<tr>
<td>EMG 900–II</td>
<td>16.09</td>
<td>22.73</td>
<td>61.18</td>
</tr>
<tr>
<td>EMG 900–III</td>
<td>16.86</td>
<td>19.05</td>
<td>64.10</td>
</tr>
<tr>
<td>EMG 900–IV</td>
<td>15.39</td>
<td>13.04</td>
<td>71.56</td>
</tr>
<tr>
<td>EMG 900–V</td>
<td>16.09</td>
<td>13.64</td>
<td>70.27</td>
</tr>
<tr>
<td>EMG 900–VI</td>
<td>16.86</td>
<td>14.29</td>
<td>68.86</td>
</tr>
<tr>
<td>EMG 905</td>
<td>7.8</td>
<td>13</td>
<td>79.2</td>
</tr>
</tbody>
</table>
4.2 Transmission Electron Microscopy of Magnetic Fluids

Figures 4.1 gives a sample TEM image of the magnetic particles in the EMG 901 ferrofluid.

![TEM image of diluted EMG 901 ferrofluid.](image)

**Figure 4.1** TEM image of diluted EMG 901 ferrofluid.

A total of ten TEM images were used for each sample (EMG 900 I–VI, EMG 901, and EMG 905). The particle sizes were determined using ImageJ software. This data was then histogrammed using SigmaPlot and fitted to the log–normal distribution (Figures 4.2–4.4).
Figure 4.2 Histogram of particles sizes fitted to the log–normal distribution for EMG901.

Figure 4.3 Histogram of particles sizes fitted to the log–normal distribution for EMG 900.
Figure 4.4 Histogram of particles sizes fitted to the log-normal distribution for EMG 905.

From the log-normal distribution the average particle size and particle size uncertainty was determined (Table 2).

Table 3 TEM histogram results for all the magnetic fluids employed in this study.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Particle size (nm)</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMG 900 (I–VI)</td>
<td>8.09</td>
<td>0.28</td>
</tr>
<tr>
<td>EMG 901</td>
<td>8.73</td>
<td>.74</td>
</tr>
<tr>
<td>EMG 905</td>
<td>10.97</td>
<td>0.29</td>
</tr>
</tbody>
</table>
4.3 X–ray Diffraction of Magnetic Fluids

X–ray diffraction of powder samples was used to determine the particle size and type of iron oxide crystal. Comparing the results of XRD data to the literature, the peak at 30.5 in Figure 4.5 corresponds to Fe$_3$O$_4$ (220).

![X–ray diffraction peak (220) from EMG 900 ferrofluid fitted with a Gaussian function to determine particle size.](image)

**Figure 4.5** X–ray diffraction peak (220) from EMG 900 ferrofluid fitted with a Gaussian function to determine particle size.

By fitting the (220) peaks of each ferrofluid sample to a Gaussian distribution, the particle size can be calculated (Table 4). This analysis (including the use of the Scherrer equation) has one several limitation. The crystal should be stress–free (which is not the case since the particles can be made by high energy ball milling). The crystal should be cubic and spherical (while TEM images show that the particles are not spherical). In the literature, the (220) peak is most prominently used due to its relative intensity. But, to accurately determine the particle size one needs to determine the strain on the crystal...
(by determining the broadening from each peak) to ensure strain effects are not present.

In Figure 4.1 one can observe that the particles are not perfect spheres. Thus, one must choose diffraction peaks corresponding to the long and short axes of the material to obtain accurate particle sizes. This cannot be done without a full crystallographic analysis of the material.

**Table 4** Particle size for each sample using TEM and X–ray diffraction.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Particle size TEM (nm)</th>
<th>Particle size X–ray (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMG 900 (I–VI)</td>
<td>8.09</td>
<td>13.55</td>
</tr>
<tr>
<td>EMG 901</td>
<td>8.73</td>
<td>14.46</td>
</tr>
<tr>
<td>EMG 905</td>
<td>10.97</td>
<td>14.69</td>
</tr>
</tbody>
</table>

The X–ray and TEM results do not agree. The reason for this disagreement is that each X–ray diffractometer has a certain offset uncertainty that needs to be accounted for. For this, a crystal of known size must be used so that the offset can be corrected to ensure that the Scherrer equation gives the correct crystal size.

**4.4 Determination of Surfactant**

To determine the type of surfactant used in the EMG series ferrofluids, infrared spectroscopy (IR), and nuclear magnetic resonance (NMR) were run. Figures 4.6–4.9 show the IR spectra of hexane, paraffin oil, a fatty acid (Oleic acid), and finally the IR spectra of EMG 900.
Figure 4.6 FTIR spectrum of hexane.

Figure 4.7 FTIR spectrum of paraffin oil.
Figure 4.8 FTIR spectrum of Oleic acid.

Figure 4.9 FTIR spectrum of EMG 900.

One observation is that the paraffin oil and hexane have three nearly identical peaks at 1467 cm\(^{-1}\) (C–H bending), 1376 cm\(^{-1}\) (C–H bending), and 2950 cm\(^{-1}\) (C–H
stretching). This leads us to conclude that the paraffin oil is a long chain hydrocarbon. Initially Ferrotec informed us that the surfactant they use is a long chain fatty acid. All fatty acids have an aliphatic chain attached to a carboxylic acid. Figure 4.8 shows a sample fatty acid (Oleic acid). The strong peak at 1700 cm\(^{-1}\) corresponds to C=O. The other three peaks at 1467 cm\(^{-1}\), 1376 cm\(^{-1}\), and 2950 cm\(^{-1}\) are also present due to the aliphatic chain attached to the carboxylic acid in Oleic acid.

Figure 4.9 shows the peaks corresponding to C−H stretching (2898 cm\(^{-1}\) and 2813 cm\(^{-1}\)) and one peak corresponding to C−H bending (1425 cm\(^{-1}\)). In Figure 4.9 a strong absorption at 560 cm\(^{-1}\) corresponding to Fe−O is observed. The IR of EMG 900 does not show the C=O peak. This means that the surfactant in EMG 900 is not a fatty acid but is most likely a long aliphatic chain (similar to paraffin oil).

The NMR spectra of the ferrofluid sample are more of a challenge than IR due to the magnetic particles inside the sample. Figures 4.10 and 4.11 is the NMR spectra of hexane and EMG 900 filtered using a magnet.
The NMR spectra for hexane (Figure 4.10) and EMG 900 (Figure 4.11) are nearly identical. The EMG 900 sample was made by adding hexane to the sample and
magnetically separating out most of the magnetic particles. The resulting liquid was faint brown, signifying that there was still some magnetic particles in the fluid (ideally there should be some surfactant in the solution as well). Both Figures 4.10 and 4.11 show chemical shifts at 0.9 ppm (alkyl primary) and 1.29 ppm (alkyl secondary) signifying that the surfactant is most likely a hydrocarbon (the CDCl$_3$ peak is at 7.27 ppm and is omitted for clarity). The magnetic particles caused some broadening of the signal in Figure 4.11 which is explained by Naginova et al.$^{151,152}$
CHAPTER V
MAGNETORHEOLOGICAL BEHAVIOR OF FERROFLUIDS
INVESTIGATED BY CONE–AND–PLATE AND PARALLEL–PLATE RHEOMETERS

5.1 Introduction

Several investigators\textsuperscript{153-155} have used parallel–plate rheometers to test the rheological behavior of magnetorheological fluids and ferrofluids. Few investigators have used cone–and–plate rheometers to determine the rheological behavior of magnetorheological fluids and ferrofluids. There are two main reasons for this. The first reason is to control the film thickness in the rheometer (for cone–and–plate rheometers, the film thickness is determined by the truncation of the cone and the angle of the cone). The second reason is the likelihood that the magnetic field would not be homogeneous in a cone–and–plate fixture.

Using a hall probe to measure the magnetic field radially from the center of the measuring fixture, it was found that the homogeneity of the magnetic field using the cone–and–plate fixture was nearly identical to the magnetic field homogeneity using the parallel–plate fixture.
To determine if there was any difference between cone–and–plate and parallel–plate rheometers a commercially available magneto–rheological (MR) fluid (Basonetic 2040 from BASF) was used. The reason we chose a MR fluid is that the MR fluids are specifically designed to give a large rheological response to applied magnetic fields. This large rheological response will give a more accurate comparison between cone–and–plate and parallel–plate rheometers. The transient shear flow experiments using the cone–and–plate fixture gave a different steady state shear stress than the transient shear flow experiments using the parallel–plate fixture. In both experiments (cone–and–plate and parallel–plate) a yield stress was observed and shear thinning was observed as the magnetic fields increased. Both of which can be attributed to aggregation or chain formation as the magnetic field increased. In this study all rheological measurements were conducted at room temperature.

5.2 Field Homogeneity of Parallel–Plate and Cone–and–Plate Configuration

The magnetic field can be determined as a function of the radial distance from the center of the cone (in cone–and–plate fixture) or plate (in parallel–plate fixture). Figures 5.1 and 5.2 show the magnetic field of a parallel–plate and cone–and–plate rheometer measured radially outwards from the center of the cone or plate. It is worth noting that this experiment was carried out with a magnetic probe measuring 2 mm across, so that each data point is an average magnetic field through a 2 mm probe.
Figure 5.1 Magnetic field versus radial distance from center of parallel–plate fixture at various electric currents (Amperes): (●) 0.1, (○) 0.5, (▼) 1, and (△) 1.5.

Figure 5.2 Magnetic field versus radial distance from center of cone–and–plate fixture at various electric currents (Amperes): (●) 0.1, (○) 0.5, (▼) 1, and (△) 1.5.
As can be seen from Figures 5.1 and 5.2 the magnetic field stays relatively uniform, for both parallel–plate and cone–and–plate fixture. One note is that at higher magnetic fields, the field for both parallel–plate and cone–and–plate fixture begins to fluctuate, depending on the position from the center. For this reason all of the rheological data was not measured above 1400 Oe. In most cases the magnetic field was below 1000 Oe.

5.3 Comparison of the Rheological Behavior of MR Fluid Between the Cone–and–Plate and Parallel–Plate Data.

The MR fluid used was a 24 vol. % suspension of micron–sized carbonyl iron powder. These particles are ferromagnetic due to the particles having a remanence magnetization (therefore these particles have hysteresis when one measures the magnetization versus applied magnetic field). Due to the 24 vol. % concentration of magnetic particles, since the system is particle filled, it would be expected that at \( H = 0 \) Oe, there should be some initial yield stress.

Transient shear stress was measured as a function of time, for which the torque was monitored as a function of time from startup until the torque reached steady state. From the torque, the steady–state shear stress (\( \sigma \)) and the stress growth function (\( \sigma^+ \)) for each shear rate and magnetic field were calculated. Figure 5.3 shows a plot of \( \sigma^+ \) versus shear strain (\( \dot{\gamma} t \)) at \( H = 0 \) at \( \dot{\gamma} = 1 \) s\(^{-1} \).
**Figure 5.3** Plot of $\sigma^+$ versus $\dot{\gamma}t$ for MR fluid at 24% using a cone–and–plate fixture at $\dot{\gamma} = 1 \text{ s}^{-1}$ at $H = 0 \text{ Oe}$.

**Figure 5.4** Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid using a parallel–plate fixture at $H = 0 \text{ Oe}$. 
Figure 5.5 Plots of yield stress versus magnetic field for 24% MR fluid using a parallel–plate fixture.

Figure 5.6 Plots of yield stress versus magnetic field for 24% MR fluid using a cone–and–plate fixture.
In Figure 5.3 $\sigma^+$ decreases to a steady-state value. This steady-state value is the steady-state shear stress ($\sigma$). Then, $\sigma$ is plotted against $\dot{\gamma}$ as shown in Figure 5.4. Extrapolating the shear stress to zero shear rate one can determine the yield stress of the material as a function of the applied magnetic field.

It can be seen from Figures 5.5 and 5.6 that the yield stress is different when measured using a parallel-plate fixture or a cone-and-plate fixture. Since there is no inhomogeneity of the magnetic field, as shown in Figures 5.1 and 5.2, this difference in yield stress observed in Figures 5.5 and 5.6 is entirely due to the difference in the measuring fixture employed (i.e. parallel-plate versus cone-and-plate fixtures).

5.4 Shear Stress and Yield Stress for MR Fluid with Increasing Particle Concentration.

Transient shear flow experiments were run using a cone-and-plate fixture for two other concentrations of MR fluid. Figures 5.7 and 5.8 show the yield stress for the 30% and 40% concentration MR fluids employed in this study (the $\sigma$ versus $\dot{\gamma}$ plots for the 40% and 30% concentration MR fluids are in Appendix B Figures 1B through 13B).
Figure 5.7 Plots of yield stress versus magnetic field for 30% MR fluid using a cone–
and–plate fixture.

Figure 5.8 Plots of yield stress versus magnetic field for 40% MR fluid using a cone–
and–plate fixture.
Comparing the 250 Oe data points in Figures 5.7 and 5.8 one observes that the 30% MR fluid has a lower value of yield stress than the 40% MR fluid value. This is attributed to the fact that the system is more filled and has more particles interacting (or more chains forming) with an increase in the particle concentration.

5.5 Viscosity of MR Fluids Under Shearing

If agglomeration occurs, one should expect that the viscosity should decrease as the shear rate increases (as the shear rate increases more chains begin to break leading to a decrease in the viscosity). Under shear flow, some of the chains might break, but not all of them. As the shear rate is increased, more of the chains will break. Since these chains affect the viscosity, it is easy to observe that as the chains break one should see the viscosity decrease. Figures 5.9 and 5.10 give plots of viscosity ($\eta$) versus shear rate ($\dot{\gamma}$) for the 24% MR fluid at two magnetic fields (the remaining $\eta$ versus $\dot{\gamma}$ plots are given in Figures 14B through 21B of Appendix B).
Figure 5.9 Plots of $\eta$ versus $\dot{\gamma}$ for 24% MR fluid at $H = 0$ Oe.

Figure 5.10 Plots of $\eta$ versus $\dot{\gamma}$ for 24% MR fluid at $H = 100$ Oe.
Figures 5.9 and 5.10 (along with Figures 14B to 21B in Appendix B) all have one thing in common. As the shear rate increases (from 0.1 to 1 or from 1 to 5 s\(^{-1}\)) the viscosity rapidly decreases. What is taking place in the fluid is initially the weakly interacting particles begin to break apart (as shown in the plots of viscosity versus shear rate). The strongly interacting particles remain essentially connected but as the shear rate increases these particles begin to break apart as well (as shown by the slow decrease in viscosity at higher shear rates).

At zero magnetic field we still observe shear thinning behavior. This is due to the particles initially having a remnant magnetization and to it being a filled system. The remnant magnetization causes the particles to interact even under no applied magnetic field.

5.6 Concluding Remarks

It was found (Figures 5.1 and 5.2) that the magnetic field measured radially from the center of both the cone–and–plate and parallel–plate fixtures was fairly uniform. The difference between the cone–and–plate and parallel–plate rheometers was investigated and it was found that the cone–and–plate rheometer gave a larger shear stress than the parallel–plate rheometer (at the same applied magnetic field).

One question that must be answered is why the parallel–plate fixture gave rise to a lower shear stress than the cone–and–plate fixture. This is attributed to how the instrument measures the shear rate. The shear rate in the parallel–plate fixture varies across the radius of the plate from zero at the center of the plate to a maximum at the outer edge of the plate. If the instrument measures the shear rate as the rotation of the
outer edge of the parallel–plate than through the radius of the plate the shear rate will be less than the outer edge. If this is true, then the lower shear stress measured by the parallel–plate fixture could be due to the average shear rate across the radius of the plate being less than the shear rate recorded by the instrument.

As for the rheological data of MR fluids at different particle concentrations (40%, 30% and 24%) one observes that the yield stress increases as the particle concentration increases (one would expect this since more particles lead to more particle–particle interactions). One also observes an increase in the shear thinning behavior of MR fluids with increasing magnetic field, leading to the conclusion that an increase in shear rate induces more particle breakage of their aggregates. The yield stress and shear thinning behavior at zero magnetic field is attributed to the fact that the magnetic particles in a MR fluid have a remnant magnetization leading to particle–particle interactions even under no applied magnetic field. Once the magnetic field is applied, all of the particles in a MR fluid begin to interact giving rise to a higher yield stress and a more pronounced shear thinning behavior.

We had to be careful in obtaining the data presented in this chapter. One problem that arose was that at very high magnetic fields the shear stress decreased very abruptly. This is most likely due to a lubrication effect. This lubrication effect is caused by the aggregation of magnetic particles leaving the carrier liquid (Poly–α–Olefin) free to move to the interface between the MR fluid and the inner surface of the cone–and–plate fixture. Once this happens, the rheometer essentially measures the viscosity of the carrier liquid and not the viscosity of the MR fluid.
6.1 Introduction

In this study, the magnetic fluids shown in Table 2 in Chapter IV were used to investigate the effect excess surfactant (excess surfactant defined as the surfactant that is not bound to the magnetic particles) has on the optical and rheological behaviors of oil–based ferrofluids. There are two rationales behind this research. The first rationale is to observe the effect film thickness has on the optical behavior of oil–based ferrofluids. It was found that films with thickness below 25 µm have an increasing birefringence (which is most likely due to interactions between the fluid and the glass). Once the films are more than 25 µm thick the birefringence and dichroism appear to remain unchanged as the film thickness increases.

The second rationale is to test the theory proposed by Taketomi\textsuperscript{53} where he theorized that the surfactant could facilitate magnetic particle micelles which could form particle chains. The optical microscopy images show no chain formation, but there appears to be shear thinning for all the magnetic fluid samples. Observing the chemical structure of the surfactant used (Chapter 4) it was found that the surfactant is most
likely a long aliphatic chain. If this is true, then this will not form micelles since it does not have a polar end (like Oleic acid does).

What is interesting is that in EMG 900–III and EMG 900–VI (recalling that EMG 900–III has 19.05 % surfactant and EMG 900–VI has 14.29 % surfactant concentration) there is a difference in birefringence, yield stress, and shear thinning behavior. EMG 900–VI has a larger birefringence, yield stress, and shear thinning than EMG 900–III. This leads us to speculate that with increasing the unbound surfactant concentration chain formation becomes more hindered than without the excess unbound surfactant as evidence by the higher birefringence, observable yield stress, and increased shear thinning. Since there is no visible chain formation observed by optical microscopy this also leads us to speculate that any particle agglomeration that is taking place is smaller than the wavelength of visible light. The dichroism data also confirms this due to the increased absorption in the magnetic field direction and the decrease in absorption in the transverse direction.

6.2 Effect of Surfactant on the Dichroism and Birefringence of Oil–Based Ferrofluids with Increasing Surfactant Concentration.

Using ferrofluids EMG 900–I through EMG 900–VI the effect of surfactant on the dichroism and birefringence was investigated. The compositions of these samples are given in Table 2. The samples are broken down as follows: EMG 900–I and EMG 900–IV, EMG 900–II and EMG 900–V, and EMG 900–III and EMG 900–VI. Each of these samples has the same nanoparticle concentration and particle size, but they only differ in surfactant concentration.
Using the samples mentioned above the dichroism was investigated using the setup given in Figure 2.8 without the analyzer. For clarity the resulting birefringence is plotted below the dichroism data.

![Normalized Transmission vs Film Thickness](image)

**Figure 6.1** Normalized transmission versus film thickness for; EMG 900−I (●) ordinary, (○) extraordinary and EMG 900−IV (▼) ordinary, and (△) extraordinary.

Figure 6.1 shows that the normalized transmission for EMG 900−I and IV overlap in both the ordinary (solid) and extraordinary (open) configurations. This result suggests that the excess surfactant plays little role. By observing the birefringence data given in Figures 6.2−6.4 one observes that as the thickness increases the birefringence decreases. There are two main mechanisms for the dichroism and birefringence of ferrofluids. The first is particle chain formation and the second is Rayleigh scattering. Figures 6.5 and 6.6 also show that the excess surfactant plays no role in the normalized transmission data. Analysis of these two phenomena (dichroism and birefringence) will be completed later.
Figure 6.2 Birefringence versus film thickness for (●)EMG 900–IV and (○)EMG 900–I.

Figure 6.3 Birefringence versus film thickness for (●)EMG 900–II and (○)EMG 900–V.
Figure 6.4  Birefringence versus film thickness for (●) EMG 900–III and (○) EMG 900–VI.

Figure 6.5  Normalized transmission versus film thickness for; EMG 900–II (○) ordinary, (●) extraordinary and EMG 900–V (△) ordinary, and (▼) extraordinary.
Figure 6.6 Normalized Transmission versus film thickness for; EMG 900–III (●) ordinary, (○) extraordinary and EMG 900–VI (▼) ordinary, and (△) extraordinary.

Since Figures 6.1, 6.5, and 6.6 show similar trends (the normalized transmission overlaps for each fluid set) one can generalize that the normalized transmission appears to be independent of the surfactant concentration. There are several reasons for this:

1) The unbound surfactant has no effect on the chain formation.

2) The unbound surfactant does have an effect, but the particles are so small that chains do not form at all.

3) The micelles are already forming and the extra added surfactant is not creating any more micelles.

The birefringence data does not add much information to differentiate what mechanism plays a role, if any (Figures 6.2 and 6.3). It appears that there could be a
difference in birefringence between EMG 900–III and EMG 900–VI (Figure 6.4). These two have a difference in surfactant concentration of 5%. This could be due to a hinderance of chain formation. The birefringence appears to have a strong thickness dependence which could be due to interactions at the interface between the glass and the ferrofluid thin film. Since the particle concentrations are all fairly similar, the birefringence at larger film thicknesses are all roughly the same (except for EMG 900–III and EMG 900–VI).

Optical micrographs of EMG 900–II at two magnetic fields are shown in Figures 6.7 and 6.8, while Figures 6.9 and 6.10 show optical micrographs of EMG 900–V at two magnetic fields.

Figure 6.7 Optical micrograph of EMG 900–II at H = 0 Oe and film thickness of 25 µm.
Figure 6.8 Optical micrograph of EMG 900–II at $H = 1420$ Oe and film thickness of 25 µm.

Figure 6.9 Optical micrograph of EMG 900–V at $H = 0$ Oe and film thickness of 51 µm.
Figure 6.10 Optical micrograph of EMG 900–V at H = 1420 Oe and film thickness of 51 µm.

As can be observed from Figures 6.7 through 6.10 there appears to be no evidence of particles (indicating the nanoparticles are very well dispersed) or of chain formation under applied magnetic fields.

6.3 Yield Stress of Oil–Based Ferrofluid with Increasing Surfactant Concentration

To determine the mechanism for the dichroism and birefringence of these ferrofluids, rheological experiments were conducted. By determining the yield stress of these fluids, we investigated if chain formation happened. If chain formation occurred, then the unbound surfactant had no effect on the chain formation. However, if no chains formed (i.e. no yield stress), then either the surfactant does have an effect (but the particles are so small that chains do not form) or the extra added surfactant does not prepare any more micelles.
Figure 6.11 gives plots of shear stress versus shear rate for EMG 900–VI, and Figures 22B through 30B in Appendix B give plots of shear stress versus shear rate for EMG 900–IV, EMG 900–II, and EMG 900–V.

**Figure 6.11** Plots of $\sigma$ versus $\gamma$ for EMG 900–VI at $H = 0$ Oe.
Figure 6.12 Plots of yield stress versus magnetic field for EMG 900–III.
Figure 6.13 Plots of yield stress versus magnetic field for EMG 900–II.

![Graph of yield stress versus magnetic field for EMG 900–II.](image)

Figure 6.14 Plots of yield stress versus magnetic field for EMG 900–VI.

![Graph of yield stress versus magnetic field for EMG 900–VI.](image)

Figure 6.15 Plots of yield stress versus magnetic field for EMG 900–V.
One can observe that the ferrofluids with added surfactant (Figures 6.12 and 6.13) have no discernible yield stress (within experimental uncertainty). The diluted ferrofluids (diluted to match the particle concentration of the added surfactant ferrofluid) do have a very small yield stress (on the order of 0.35 Pa in Figure 6.14 and 0.4 Pa in Figures 6.15). The reason for the large error bars in the above data is due to the fact that the torque measured by the instrument was on the order of the instrument uncertainty. Figure 6.16 shows an example of plots of stress growth versus shear strain of a typical experimental run using these ferrofluids.

![Figure 6.16 Plots of σ
+ versus \( \dot{\gamma} t \) for EMG 900–III at \( H = 100 \text{ Oe} \).](image)

One can compare the data of Figure 6.16 with Figure 5.3 and conclude that for the ferrofluid (Figure 6.16) there is no maximum in stress growth (indicative of interactions between particles) and the scale of the shear stress (for the MR fluid shown in Figure 5.3...
the shear stress is 10 Pa without an applied magnetic field and for the ferrofluid 3 Pa at a magnetic field of 500 Oe).

6.4 Determination of the Viscosity of Ferrofluids

One would expect that since the ferrofluids with excess surfactant have no yield stress (within experimental uncertainty), that there should be almost no shear thinning of the ferrofluids. Figures 6.17 through 6.21 give plots of $\eta$ versus $\dot{\gamma}$ for EMG 900–VI (at $H = 0$ Oe and $H = 500$ Oe) and EMG 900–III (at $H = 500$ Oe) along with EMG 900–V (at $H = 500$ Oe) and EMG 900–II (at $H = 500$ Oe).

Figure 6.17 Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900–VI at $H = 0$ Oe.
Figure 6.18 Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900–VI at $H = 500$ Oe.

Figure 6.19 Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900–III at $H = 500$ Oe.
Figure 6.20 Plots of \( \eta \) versus \( \dot{\gamma} \) for EMG 900–V at \( H = 500 \text{ Oe} \).

Figure 6.21 Plots of \( \eta \) versus \( \dot{\gamma} \) for EMG 900–II at \( H = 500 \text{ Oe} \).
Figures 6.17 through 6.21 show that viscosity decreases as shear rate increases, very similar to that shown for the MR fluid. The main difference between them is that the magnitude of the viscosity (for the ferrofluid the decrease is only a few pascals whereas for the MR fluid it can be several orders of magnitude higher). Another explanation for the shear thinning behavior observed is that the particles could have some small remnant magnetization (there could be some larger particles present due to the particle size distribution being fairly broad).

One observes that for the fluid with increased surfactant concentration (Figures 6.19 and 6.21) the viscosity is higher than that for the fluids diluted to the same particle concentration (Figures 6.18 and 6.20). One explanation for this is that the surfactant is a long aliphatic chain. If one increases the amount of this surfactant in the fluid one should expect the viscosity to increase (since the carrier liquid is a low molecular weight aliphatic chain).

6.5 Concluding Remarks

There were two main questions posed in this research. The first was the effect film thickness has on the optical behavior of oil–based ferrofluids and the second was the effect the surfactant has on the optical and rheological behavior of these fluids.

As the film thickness increases, the normalized transmission for both the ordinary and extraordinary ray stays relatively constant above a thickness of 25 µm. One also observes that the birefringence stays relatively constant above the thickness of 25 µm. As mentioned previously the increase in birefringence observed in Figures 6.2–6.4 for films under 25 µm could be due to possible interactions between the glass and the fluid. The
problem with this conclusion is that for most optical studies of ferrofluids that are not
diluted the typical film thickness is under 25 µm and therefore one should take into
account the effect the sample cell has on the optical data.

The second question posed is how the surfactant affects the optical and
rheological behavior of oil–based ferrofluids. From the optical micrographs one can rule
out large chain aggregates forming even under relatively high magnetic fields. From the
dichroism results one can observes that the ordinary ray's transmission is greater than 1
(meaning that as the applied magnetic field increases there is less light being absorbed).
This normalized transmission for the ordinary ray being greater than 1 could be due to
chains forming in the extraordinary direction giving the ordinary direction less scattering.

From the rheological data one can also observe that the diluted ferrofluids have a
small yield stress (Figures 6.13 and 6.15) whereas the added surfactant ferrofluids do not
(Figures 6.12 and 6.14). Even though the optical data shows that the normalized
transmission for the ordinary ray is greater than 1 there is still some chain formation
taking place (as evidenced from the shear thinning behavior and extraordinary ray
intensity decreasing). What is interesting is that even though more chain formation is
taking place for the diluted ferrofluid than the added surfactant ferrofluid (as evidenced
by the rheological data) the optical data for each fluid show that they are identical (except
for the case of EMG 900–III and EMG 900–VI). The difference between EMG 900–III
and EMG 900–VI is attributed to the excess surfactant in EMG 900–III hindering chain
formation while the particle concentrations in all other fluids was less than the particle
concentration in EMG 900–VI. This could have caused more chain formation.
To understand why the optical data shows that the diluted and added surfactant have similar optical behavior while the rheological behavior are different, one needs to look at the optical micrographs of each ferrofluid. Recall that Figures 6.8 through 6.10 show optical micrographs of EMG 900–II and EMG 900–V (the optical micrographs for the four remaining samples look identical to these although not presented here). In the EMG 900 series fluids no chain formation was observed even at 1400 Oe. Since the light source used was a HeNe laser having the wavelength of 632 nm the laser is not sensitive enough to detect small particle chains where the chain's thickness is less than 632 nm. This means that for surfactant stabilized ferrofluids birefringence and dichroism is not a good technique to determine chain formation (unless the incident light's wavelength is a few nanometers or lower).
CHAPTER VII

DICHOISM, BIREFRINGENCE, AND RHEOLOGICAL BEHAVIORS OF FILTERED OIL–BASED FERROFLUIDS.

7.1 Introduction

The optical and rheological behaviors of oil–based ferrofluids depend on the particle size and surfactant type/concentration. For this study, EMG 905 ferrofluid underwent magnetic separation to remove the smaller particles as well as the excess surfactant. The experimental observations of the filtered EMG 905 films show small agglomeration on the order of a micron in filtered fluid. Even with sonication of over an hour, these micron–sized agglomerates were not removed. Based on the NMR and IR spectroscopy of the surfactant it was concluded that the surfactant was a long aliphatic hydrocarbon (so the surfactant must be wrapped around the particle and not bound to the particle). Since the filtering was done with hexane there was a strong chance that a lot of the surfactant, which was wrapped around the particles, was removed giving rise to this degree of agglomeration. The rationale behind this study was in two parts. The first part was to investigate the chain formation of a ferrofluid with low surfactant concentration. The second part was to investigate how small particle agglomerates play a role in the optical and rheological behaviors of oil–based ferrofluids. Since most ferrofluids contain certain amount of agglomerates, this was of a practical concern, since in most synthesized ferrofluids it is impossible to ensure that none of the particles are agglomerated.
The dichroism of the filtered EMG 905 shows a decrease in both the ordinary and extraordinary ray while EMG 905 shows only a decrease in intensity of the extraordinary ray. For the filtered EMG 905 this shows that in both directions (parallel to magnetic field and perpendicular) there are agglomerations that are absorbing or scattering the light. Due to the optical microscopy images of the filtered EMG 905, it is speculated that the absorption of the extraordinary ray is due to the particle chains forming in the magnetic field direction, while the absorption in the ordinary direction is due to the thickness of the particle chains. Since EMG 905 does not have absorption in the ordinary direction it is speculated that the chains are too small to be detected by visible light (confirmed by the optical microscopy images of EMG 905). The yield stress and viscosity data confirm aggregation in the filtered EMG 905 and little or no aggregation in EMG 905.

7.2 Preparation of Large Particle Ferrofluid

The EMG 905 ferrofluid was magnetically separated using a permanent magnet with a magnetic field of 7000 Gauss. EMG 905 was chosen due to its larger average particle size measured by TEM and X-ray. The sample was diluted and placed on the magnet. After 24 hours the resulting fluid separated with the large particles on the bottom. The top portion of the liquid (which contained the small particles that did not interact strongly with the magnetic field) was removed and the bottom portion of the liquid was allowed to dry. After doing this several times with several samples the resulting dry particles were weighed and were resuspended to 7.8 % by volume (to match the particle concentration of EMG 905). Three different film thicknesses were prepared (31 µm, 55 µm, and 95 µm) and they were used for the optical microscopy, dichroism,
and birefringence experiments. After each experiment the large particle thin films were sonicated and imaged with the microscopy to ensure no structures were present in the sample before each experiment was carried out.

7.3 Optical Microscopy, Dichroism, and Birefringence of Large Particle Ferrofluid

In the following sections, we will discuss the optical behavior of each ferrofluid film and how the film thickness relates to the chain formation, dichroism, and birefringence of the thin films. In each micrograph O and E correspond to the ordinary ray direction and the extraordinary ray direction, respectively.

7.3.1 Optical Microscopy, Dichroism, and Birefringence of 31 µm Filtered Ferrofluid Film

Figures 7.1–7.6 are the optical microscopy images for the 31 µm thin film of filtered EMG 905.
Figure 7.1 Optical micrograph of a 31 µm thin film of filtered EMG 905 at 0 Oe.

Figure 7.2 Optical micrograph of a 31 µm thin film of filtered EMG 905 at 123 Oe.
**Figure 7.3** Optical micrograph of a 31 µm thin film of filtered EMG 905 at 257 Oe.

**Figure 7.4** Optical micrograph of a 31 µm thin film of filtered EMG 905 at 449 Oe.
Figures 7.1–7.6 show that as the magnetic field is increased the particles begin to align in the filtered EMG 905 sample. From 0 to 123 Gauss of applied magnetic field the
particles begin to form chains that begin to combine as the magnetic field is increased further to 449 Gauss. Above 449 Gauss it appears that the chains stop growing and structure stays relatively constant. This is consistent with the dichroism data shown in Figure 7.7.

![Graph showing normalized transmission versus magnetic field](image)

**Figure 7.7** Plots of normalized transmission versus magnetic field for 31 µm thin film of filtered EMG 905 for (•) extraordinary and (○) ordinary ray.

For both the extraordinary and ordinary ray, the normalized transmission decreases as the magnetic field increases. This could be due to the absorption of light in both the chain length direction (extraordinary ray) and the chain thickness direction (ordinary ray). Also, at roughly 450 Gauss, the normalized transmission shows a plateau for both the ordinary and extraordinary rays due to no new chains forming or combining.
at these magnetic fields shown in Figures 7.3–7.6. Figure 7.8 gives birefringence as a function of magnetic field for 31 µm thin film of filtered EMG 905.

![Figure 7.8 Plots of birefringence versus magnetic field 31 µm thin film of filtered EMG 905.](image)

One can observe that as the magnetic field increases, so does the birefringence. From observing the optical micrographs one can conclude that this must be due (at least in part) to the formation of magnetic particle chains at the magnetic field levels.
7.3.2 Optical Microscopy, Dichroism, and Birefringence of 55 µm Thin Film of Filtered Ferrofluid

Figures 7.9–7.14 give the optical micrographs of the 55 µm thin film of filtered ferrofluid.

Figure 7.9 Optical micrograph of 55 µm thin film of filtered EMG 905 at 0 Oe.
Figure 7.10 Optical micrograph of 55 µm thin film of filtered EMG 905 at 123 Oe.

Figure 7.11 Optical micrograph of 55 µm thin film of filtered EMG 905 at 257 Oe.
**Figure 7.12** Optical micrograph of 55 µm thin film of filtered EMG 905 at 449 Oe.

**Figure 7.13** Optical micrograph of 55 µm thin film of filtered EMG 905 at 991 Oe.
Figures 7.9–7.14 show that as the magnetic field increases for the 55 µm film, the chains initially form, then these small chains begin to form larger chains. Even at higher magnetic fields (Figure 7.14) the chains continue to combine and form. Plots of normalized transmission versus magnetic field, given in Figure 7.15, also show that there is no saturation.

There can be a chance that the banded structures shown in the micrographs in this chapter could be Moire fringes. Moire fringes are beat patterns resulting from the diffraction of two “grates” slightly tilted, giving rise to a banded structure. Moire fringes could be formed by particle chains (chains smaller than the wavelength of light) that are not perfectly aligned with the magnetic field which diffracts light. This diffracted light would produce a banded structure referred to as Moire fringes. In Figures 7.1–7.6 and
7.9–7.14 Moire fringes could be happening, but we think that the bands are due to particle agglomeration.

Figure 7.15 Plots of normalized transmission versus magnetic field for 55 µm thin film of filtered EMG 905: (●) extraordinary and (○) ordinary ray.

One also observes from Figure 7.15 and 7.16 that the normalized transmission and birefringence do not saturate. This is a particularly interesting phenomenon since the birefringence and normalized transmission in Figures 7.7 and 7.8 are saturated. By comparing Figures 7.14 with Figure 7.6 one observes a very large difference, whereas in Figure 7.6 there appears to be a lot of chains (both large chains and smaller chains) while in Figure 7.14 there appears to be mostly only large chains. One also observes that the structure saturates for the 31 µm film, but one does not observe this taking place for the 55 µm film.
Figure 7.16 Plots of birefringence versus magnetic field for 55 µm thin film of filtered EMG 905.

7.3.3 Optical Microscopy, Dichroism, and Birefringence of 95 µm Film

Figure 7.17 Optical micrograph of 95 µm thin film of filtered EMG 905 at 0 Oe.
Figure 7.18 Optical micrograph of 95 µm thin film of filtered EMG 905 at 123 Oe.

Figure 7.19 Optical micrograph of 95 µm thin film of filtered EMG 905 at 991 Oe.
Figures 7.17–7.19 show some structure formation as the magnetic field is increased from 0 Oe to 991 Oe. An interesting observation with Figure 7.20 is that when the filtered EMG 905 is in the magnetic field one can observe the edges near the magnet getting darker. After applying the 1453 Oe magnetic field and observing the film one observes an inhomogeneity in the color of the film. Initially the film was all black, but when removing the film from the 1453 Oe magnetic field one observes a slightly lighter area in the center of the film surrounded by black on the edges (these edges were where the magnet was placed). This observation leads us to conclude that the reason why we were unable to observe significant chain formation in the lower field films was the amount of particles blocking nearly all of the incident light, but at higher magnetic fields these particles moved towards the magnet. This observation explains the normalized transmission data given in Figure 7.21.
Figure 7.21 Plots of normalized transmission versus magnetic field for 95 µm thin film of filtered EMG 905: (●) extraordinary and (○) ordinary ray.

The data for the ferrofluids 35 and 55 µm thick agree with the optical microscopy images from other groups. Most of the papers that mention film thickness have it less than 20 µm. Figure 7.21 shows that the normalized transmission increases as the magnetic field increases. Along with chain formation the particles form dense phases and these phases could begin to move towards the edges. This would prepare a low particle zone which would explain the normalized transmission increasing with applied magnetic field (more particles would form into these blocks and move towards the edge). This phenomenon was not observed with any other ferrofluid film employed in all the previous studies.
Horng et al.\textsuperscript{44} found that as the film thickness increases the transmission at zero magnetic field decreases. They defined the normalized intensity as the intensity the photodector reads with the sample in, divided by the intensity of the light through no sample. Recall that we are determining the normalized transmission by dividing the intensity the photodector reads at an applied magnetic field divided by the intensity of the sample with no magnetic field. If we replot Figures 7.7, 7.15, and 7.21 defining the normalized intensity as Horng et al.\textsuperscript{44} did we obtain Figures 7.23 and 7.24 (varying film thickness but keeping polarizer direction constant).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Plots of birefringence versus magnetic field for 95 \textmu m thin film of filtered EMG 905.}
\end{figure}
Figure 7.23 Plots of normalized intensity versus magnetic field for extraordinary ray for different film thicknesses of filtered EMG 905: (●) 31 µm, (▼) 55 µm, and (○) 95 µm.

Figure 7.24 Plots of normalized intensity versus magnetic field for ordinary ray for different film thicknesses of filtered EMG 905: (●) 31 µm, (▼) 55 µm, and (○) 95 µm.
Figures 7.23 and 7.24 show that the 95 µm (and even the 55 µm for the ordinary ray) are within experimental uncertainty. This makes sense for the 95 µm film since the film is very thick and the signal coming to the photodetector is very low. The ordinary ray for the 55 µm film is also relatively constant (Figure 7.24) at first, but then begins to decrease with higher magnetic fields (from 449 to 1453 Oe). Figures 7.12–7.14 show that as the magnetic field increases the small chains are beginning to form larger and thicker. These thicker chains absorb more of the light in the ordinary direction. Now one needs to compare the results obtained from the filtered EMG 905 with EMG 905.

7.4 Optical Micrographs and Dichroism of EMG 905.

Figures 7.25 and 7.26 give the optical micrographs and Figure 7.27 gives dichroism data for 83 µm thin film of EMG 905. This ferrofluid film was imaged at the same magnetic fields as the filtered EMG 905 films, but due to there being no structure forming only the 0 Oe and the 1420 Oe images will be presented here.
Figure 7.25 Optical micrograph of 83 µm thin film of EMG 905 at H = 0 Oe.

Figure 7.26 Optical micrograph of 83 µm thin film of EMG 905 at H = 1420 Oe
Figure 7.27 Plots of normalized transmission versus magnetic field for 83 µm film of EMG 905: (●) ordinary ray, and (○) extraordinary ray.

The optical micrographs show that there is no visible chain formation under the applied magnetic field of 1420 Oe. The dichroism data (similar to the EMG 900 series) shows that chain formation could take place, but the thickness of the chains was smaller than the wavelength of visible light.

7.5 Yield Stress of Filtered EMG 905

Figure 7.28 give plots of shear stress versus shear rate for EMG 905 at H = 0 Oe (Figures 34B through 36B in Appendix B). Figures 37B through 42B in Appendix B give plots of shear stress versus shear rate for the filtered ferrofluid and Figures 7.29 and 7.30 give plots of yield stress versus magnetic field for the same ferrofluid.

Figure 7.28 Plots of σ versus \( \dot{\gamma} \) for EMG 905 at H = 0 Oe.
Figure 7.29 Plots of yield stress versus magnetic field for EMG 905.

Figure 7.30 Plots of yield stress versus magnetic field for filtered EMG 905.
Figure 7.29 shows that above 500 Oe one is able to observe a yield stress. This is an interesting phenomenon since the optical micrograph of EMG 905 at 1420 Oe shows no indication of chain formation (Figure 7.26). The dichroism of the EMG 905 (Figure 7.27) shows identical trends to the dichroism of the diluted and surfactant added ferrofluids discussed in Chapter 6 even at a magnetic field as high as 4000 Oe. This observation leads us to conclude that chain formation could take place in the unfiltered ferrofluid but (like in EMG 900) the chains would be short. The reason why we were able to observe a yield stress in EMG 905 and not EMG 900 could also be due to the larger average particle size in EMG 905 (measured by TEM and X–ray). This larger particle size was also the reason why we chose to remove the surfactant from EMG 905.

The filtered EMG 905 (Figure 7.30) does show chain formation through each magnetic field and one can observe the yield stress increasing as the magnetic field increases (except between 0 and 100 Oe where the yield stress stays relatively flat).

7.6 Determination of Viscosity for EMG 905 and Filtered EMG 905

Figure 7.31 and 7.32 give plots of $\eta$ versus $\dot{\gamma}$ for EMG 905 and filtered EMG 905 at $H = 350$ Oe. All of the viscosity data for EMG 905 and filtered EMG 905 were measured using the cone–and–plate configuration at 23 °C.
Figure 7.31 Plots of η versus $\dot{\gamma}$ for EMG 905 at H = 350 Oe.

Figure 7.32 Plots of η versus $\dot{\gamma}$ for filtered EMG 905 at H = 350 Oe.
At 350 Oe EMG 905 (Figure 7.31) has no shear thinning behavior which is attributed to very little chain formation (or no chain formation at all). The yield stress for EMG 905 also confirms that there is very small yield stress, meaning that very little chain formation takes place. The filtered EMG 905 at 350 Oe does show shear thinning behavior (Figure 7.32) and a more pronounced yield stress (Figure 7.30). This is an interesting conclusion since the other ferrofluids (EMG 900 series) show shear thinning even though the yield stress is nonexistent.

### 7.7 Concluding Remarks

For the filtered EMG 905 the optical microscopy images show chain formation which is confirmed by the dichroism and rheological data. The dichroism data shows a different trend from the EMG 900 series and this can be attributed to the chain formation in the EMG 900 series having shorter chains (chains having smaller thickness than the visible light spectrum). In Figures 6.13 and 6.15 of Chapter 6 one observes that the yield stress is actually comparable to that of the filtered EMG 905, which suggests that one should also observe similar optical and rheological behaviors. This does not necessarily have to be true since the ferrofluids presented in Chapter 6 have greater particle concentration and they can have a yield stress with many small–size chains (instead of the filtered EMG 905, whereas it exhibits yield stress with smaller amounts of large–particle chains).

The optical data shows that the filtered EMG 905 had more chain formation than the unfiltered fluids (EMG 905 and EMG 900 series). As observed by the optical micrographs the particle chains are larger than the wavelength of visible light, so one
would expect this. Since all of the optical samples are greater than 25 µm the data should have minimal surface effects contributing to the results.

Considering the normalized intensity (Figures 7.23 and 7.24) one can observes that as the film thickness increases the normalized intensity decreases with it (which is expected since the light has to go through more fluid). One also observes that the thicker films have very similar normalized intensities compared to the thinner film (they both decrease until a certain magnetic field then remains flat). As the magnetic field increases the normalized intensity stays relatively constant at applied magnetic fields above $H = 600$ Oe, meaning that there could be some saturation. For the largest film thickness there appears to be little change in the normalized intensity (which is due to the film being nearly opaque). For the 93 µm film (Figure 7.21) the normalized transmission actually observes to increase. It was observed that as the magnetic field increased for the 93 µm film some inhomogeneity started forming where the center of the film became lighter than the outer edges (the outer edges that were near the magnet). This observation explains the normalized transmission in Figure 7.21. From Figure 7.23 and 7.24 one can also observe that the normalized intensity for the 93 µm film is also very low, showing that there was not much light passing through the sample.
CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

In the first part of this dissertation, a series of ferrofluids were characterized to determine the surfactant type and particle size. The results of this investigation are that the surfactant was determined to be a long chain aliphatic hydrocarbon with no functional groups (due to the magnetic fluid having NMR and IR peaks similar to hexane). The particle size was determined via TEM and X–Ray and it was found that the particles are all on the order of single–domain particles (with the X–ray data having a large uncertainty due to not being able to correct for the line shift inherent in the instrument).

In the second part of this dissertation, two MR fluids were used to determine the difference between a cone–and–plate fixture and a parallel–plate fixture (both made out of titanium). To do this, the magnetic field homogeneity across the fluid gap had to be determined for both the cone–and–plate and parallel–plate fixtures. It was found that the magnetic field was very homogeneous for both the cone–and–plate and parallel–plate fixtures below H = 1400 Oe. The transient shear flow experiments run for both fixtures were compared. It was found that the cone–and–plate fixture gave larger shear stresses than the parallel–plate fixture (at the same applied magnetic field). This was attributed to the way the instrument determines the shear rate for the parallel–plate fixture. The instrument measures the shear rate as the rotation of the outer edge of the
parallel–plate. Through the radius of the plate the shear rate will be less than the outer edge. This gives a lower shear stress measured by the parallel–plate fixture due to the average shear rate across the radius of the plate being less than the shear rate recorded by the instrument.

Having confirmed that the magnetic field is uniform for the cone–and–plate fixture we prepared plots of yield stress versus magnetic field, and plots of viscosity versus shear rate. We were able to observe strong yield stress that increased as the magnetic field increased and shear thinning behavior. The increased yield stress was attributed to the formation of structures (chain formation or agglomeration) as the magnetic field increased. The shear thinning behavior is attributed to the structures in the magnetic fluid breaking (where at low shear rates the larger structures break and at higher shear rates the smaller structures break).

In the third part of this dissertation, a series of ferrofluids were prepared where the particle concentration and particle size of each fluid remained constant but the amount of surfactant in each fluid varied. There were two main questions posed in this part of the dissertation. The first was the effect of film thickness on the optical behavior of oil–based ferrofluids, and the second question was the effect surfactant has on the optical and rheological behaviors of these fluids.

It was found that with a film thickness below 25 µm the birefringence began to increase. The dichroism data shows that below the film thickness of 25 µm the ordinary ray of the normalized transmission is lower than it is above 25 µm. The extraordinary ray of the normalized transmission below 25 µm is higher than it is above 25 µm. This signifies that less chain formation took place at these thinner film thicknesses and due to
the birefringence data being larger for these thin films one can conclude that there must be something else taking place when the magnetic fluid film is thinner than 25 µm. This may lead some researchers to speculate that there might be interactions between the magnetic fluid and the glass used to encase the ferrofluid thin films. All subsequent optical data was taken at film thicknesses above 25 µm.

From the optical micrographs one can rule out large chain aggregates forming at any magnetic field used. This does not rule out small particle chain aggregates whose size is smaller than the wavelength of visible light. From the results of dichroism the ordinary ray's normalized transmission is greater than 1 and the extraordinary ray's normalized transmission is less than 1. The extraordinary ray's normalized transmission being less than 1 could be due to the chain formation in the field direction (which is the extraordinary ray direction) and the chain aggregates could be absorbing some of this light leading to a decrease in the normalized transmission. The ordinary ray's normalized transmission being greater than 1 means that less scattering is taking place in the direction perpendicular to the magnetic field. This is most likely due to the magnetic particles aligning in the extraordinary direction giving the ordinary direction fewer scatterers. Since these particle chains are thinner than the wavelength of the incident laser the laser light does not scatter giving an increase in the normalized transmission (while in the extraordinary direction the particle chains are long enough for the incident laser light to scatter giving a decrease in the normalized transmission).

The effect of surfactant on the optical and rheological behaviors of ferrofluids showed that the micelle formation proposed by Taketomi was not taking place. Due to the surfactant being a long aliphatic hydrocarbon the micelles could not form (since there
was no polar head). Most of the samples had enough surfactant in them that an addition of extra surfactant did not change the optical behavior of ferrofluid films. The rheological behavior of the samples does show a great deal of difference. For the ferrofluids with added surfactant there is no observable yield stress while the ferrofluids without added surfactant show a small yield stress. This means that the added unbound surfactant causes a hindrance to chain formation instead of forming micelles. An interesting observation is that the ferrofluids with and without added surfactant show shear thinning behavior similar to the MR fluids. This means that there should be some chain formation in all of the EMG 900–I through EMG 900–VI used, but for the ferrofluids without added surfactant the shear thinning appears to take place more abruptly (the drop in viscosity at shear rates from 1 to 5 s$^{-1}$ is higher for the ferrofluids without added surfactant). This could be a result of more chain formation in the ferrofluids without added surfactant.

In the fourth part of this dissertation we filtered out the surfactant and small particles in EMG 905 to prepare filtered EMG 905. It was found that the filtered EMG 905 had yield stress similar to that of EMG 900–V, but they had very different optical behavior (filtered EMG 905 had less than half the particle concentration of EMG 900–V) due to the absence of surfactant. One observes that for the filtered EMG 905 both the ordinary and extraordinary rays in the dichroism decrease (where the extraordinary ray is lower). This signifies that chain formation took place and that the chain thickness is large enough for the ordinary ray to be absorbed. The optical micrograph images confirm that the particle chains are large and thick enough to be observed under an optical microscope. One also observes that there is shear thinning for the filtered EMG 905 and no shear thinning for EMG 905. This is most likely tied to the presence of yield stress for
EMG 905 being zero (within experimental uncertainty) at magnetic fields up to $H = 350$ Oe.

At larger film thicknesses the normalized transmission becomes less reliable due to the low intensity of the light passing through the sample. The normalized intensity for the thicker film (93$\mu$m) shows that the intensity is very low compared to that for the thinner films. This coupled with the observation of inhomogeneities forming in the ferrofluid film as the magnetic field increased leads us to speculate that the normalized transmission of very thick films is unreliable.

It is recommended that an investigation be carried out to investigate the effect film thickness has on the optical behavior of ferrofluids having thicker films. There appears to be an optimum film thickness and it would be worth investigating this further. For this investigation optical microscopy, dichroism, and birefringence should be employed. Another issue worth investigating is to prepare a ferrofluid with a surfactant similar to Oleic acid and determine the effect unbound surfactant has on the optical and rheological behaviors of this fluid. For this investigation one would need to prepare a good quality ferrofluid (one that does not agglomerate and contains mostly single–domain particles) and add extra surfactant. In this dissertation, we found that adding unbound surfactant (where the surfactant was a long chain aliphatic hydrocarbon) decreased the chain formation. But for Oleic acid the theory by Taketomi predicts an increase in chain formation which would be evident by an increase in yield stress or a decrease in the ordinary and extraordinary ray in the dichroism study.
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APPENDICES
The theory derived by Taketomi$^{22,148}$ expressing the phase difference through a magnetic fluid starts by defining the electric field in the Y and Z direction shown in Figure 1B.

The electric field vector for the Y and Z directions is defined as:

\[ E_y = E_o \cos \beta \exp[-h_1] \sin \mu \]  \hspace{1cm} (1A)  

\[ E_z = E_o \sin \beta \exp[-h_2] \sin (\mu + \varphi) \]  \hspace{1cm} (2A)

where \( E_o \) is the initial intensity (which we define as being the same for both the y and z directions since they cancel later) \( h_1 \) and \( h_2 \) are the absorption constants defined in the text with Eq. (x), \( \mu = wt + \theta_o \) where \( w \) is the angular velocity of the light and \( \theta_o \) is a constant. When we set \( \beta = \pi/4 \) both the sin and cos term goes to \( \sqrt{2}/2 \).
Rewriting Eq. (1B) in terms of \( \sin \mu \) and expanding the \( \sin (\mu + \varphi) \) of Eq. (2B) one obtains:

\[
\sin \mu = \left( \frac{E_y}{E_o} \right) \sqrt{2} \exp[h_1]
\]  

(3A)

\[
E_x = \left( \frac{\sqrt{2}}{2} \right) E_o \exp[-h_2][ \sin (\mu) \cos \varphi + \cos (\mu) \sin \varphi]
\]  

(4A)

Since \( \cos \mu = \sqrt{1 - \sin^2 \mu} \) one can rewrite Eq. (3B) into the equivalent form of Eq. (5A).

\[
\cos \mu = \sqrt{1 - 2 \left( \frac{E_y}{E_o} \right)^2 \exp[2h_1]}
\]  

(5A)

Substituting Eqs. (5A) and (3A) into Eq. (4A) one obtains:

\[
E_x = \left( \frac{\sqrt{2}}{2} \right) E_o \exp[-h_2][ \left( \frac{E_y}{E_o} \right) \sqrt{2} \exp[h_1] \cos \varphi]
\]
\[ + \sqrt{1 - 2 \left( \frac{E_y}{E_o} \right)^2 \exp[2h_1 \sin (\varphi)]} \] (6A)

\[ \frac{E_z}{E_o} = \left( \frac{E_y}{E_o} \right) \exp[h_1 - h_2] \cos \varphi \]

\[ + (\frac{\sqrt{7}}{2}) \exp[-h_2] \sqrt{1 - 2 \left( \frac{E_y}{E_o} \right)^2 \exp[2h_1 \sin (\varphi)]} \] (7A) \[ \frac{E_z}{E_o} - \]

\[ (\frac{E_y}{E_o}) \exp[h_1 - h_2] \cos \varphi \]

\[ = (\frac{\sqrt{7}}{2}) \exp[-h_2] \sqrt{1 - 2 \left( \frac{E_y}{E_o} \right)^2 \exp[2h_1 \sin (\varphi)]} \] (8A)

Squaring both sides of Eq. (8A) one obtains

\[ (\frac{E_z}{E_o})^2 - (\frac{E_y}{E_o})^2 \exp[2(h_1 - h_2)] \cos^2 \varphi - \frac{2E_z E_y}{E_o^2} \exp[2(h_1 - h_2)] \cos \varphi = \]

\[ (\frac{1}{2}) \exp[-h_2] \left( 1 - 2 \left( \frac{E_y}{E_o} \right)^2 \exp[2h_1] \right) \sin (\varphi) \] (9A)

\[ (\frac{E_z}{E_o})^2 - (\frac{E_y}{E_o})^2 \exp[2(h_1 - h_2)] \cos^2 \varphi - \frac{2E_z E_y}{E_o^2} \exp[2(h_1 - h_2)] \cos \varphi = \]

\[ (\frac{1}{2}) \exp[-2h_2] \sin^2 \varphi - \left( \frac{E_y}{E_o} \right)^2 \exp[2(h_1 - h_2)] \sin^2 \varphi \] (10A) for convenience we will define a new variable \( x = 2(h_1-h_2) \). Dividing Eqs. (9A) and (10A) by \( \exp[x] \) and simplifying one obtains

\[ (\frac{E_z}{E_o})^2 \exp[-x] - (\frac{E_y}{E_o})^2 \exp[x] \cos^2 \varphi - \frac{2E_z E_y}{E_o^2} \cos \varphi = \]

\[ (\frac{1}{2}) \exp[-(h_1 + h_2)] \sin^2 \varphi - \left( \frac{E_y}{E_o} \right)^2 \exp[x] \sin^2 \varphi \] (11A)
\[
\left( \frac{E_x}{E_o} \right)^2 \exp[-x] - \left( \frac{E_y}{E_o} \right)^2 \left[ \exp[x] \cos^2 \varphi - \exp[x] \sin^2 \varphi \right] - \frac{2E_xE_y}{E_o^2} \cos \varphi = \\
\left( \frac{1}{2} \right) \exp[-(h_1 + h_2)] \sin^2 \varphi \quad (12A)
\]

\[
\left( \frac{E_x}{E_o} \right)^2 \exp[-x] - \left( \frac{E_y}{E_o} \right)^2 \exp[x] - \frac{2E_xE_y}{E_o^2} \cos \varphi = \\
\left( \frac{1}{2} \right) \exp[-(h_1 + h_2)] \sin^2 \varphi \quad (13A)
\]

Eq. (13B) which is the equation of the ellipse formed by Eqs. (1A) and (2A) in the \( (x, y, z) \) coordinate system. This equation obeys the general formula of an ellipse defined as

\[
Ax^2 + Cy^2 + Bxy = D \quad (14A)
\]

where \( x \) and \( y \) correspond to \( E_y \) and \( E_z \), respectfully. To determine the semi-major and semi-minor axis of the ellipse we need to define a coordinate system in such a way as the \( Bxy \) term goes to zero. The new coordinates are defined as

\[
x = r \cos (\mu + \Delta) \quad (15A)
\]

\[
y = r \cos (\mu + \Delta) \quad (16A)
\]

where \( \Delta \) is the angle of rotation to get from the old coordinates to the new coordinates.

\[
x = r \cos (\mu + \Delta) = r \cos (\mu) \cos (\Delta) - r \sin (\mu) \sin (\Delta) \quad (17A)
\]

The new coordinates are defined as \( X = r \cos \Delta \) and \( Y = r \sin \Delta \) the old coordinate \( x \) and \( y \) can be rewritten with the new coordinates \( X \) and \( Y \).

\[
x = X \cos (\Delta) - Y \sin (\Delta) \quad (18A)
\]

\[
y = X \sin (\Delta) + Y \cos (\Delta) \quad (19A)
\]
Substituting the new coordinates, Eqs. (18B) and (19B), into the generalized form of an ellipse Eq. (14B), one obtains

\[ A[X \cos (\Delta) - Y \sin (\Delta)]^2 + C[X \sin (\Delta) + Y \cos (\Delta)]^2 + B(X \cos (\Delta) - Y \sin (\Delta))(X \sin (\Delta) + Y \cos (\Delta)) = D \]  

(20A)

For clarity, Eq. (20A) will be separated into A,B, and C components:

\[ A[X^2 \cos^2 (\Delta) - 2XY \cos (\Delta) \sin (\Delta) + (Y^2 \sin^2 (\Delta))] + \]
\[ C[X^2 \sin^2 (\Delta) + 2XY \cos (\Delta) \sin (\Delta) + (Y^2 \cos^2 (\Delta))] + \]
\[ B[X^2 \cos (\Delta) \sin (\Delta) + XY \cos^2 (\Delta) - XY \sin^2 (\Delta) - Y^2 \cos (\Delta) \sin (\Delta)] \]
\[ = D \]  

(21A)

(22A)

(23A)

combining X and Y terms gives the following expressions:

\[ X^2[A \cos^2 (\Delta) + B \cos (\Delta) \sin (\Delta) + C \sin^2 (\Delta)] + \]
\[ XY[[\cos^2 (\Delta) - \sin^2 (\Delta)] - 2(A - C) \cos (\Delta) \sin (\Delta)] + \]
\[ Y^2[A \sin^2 (\Delta) - B \cos (\Delta) \sin (\Delta) + C \cos^2 (\Delta)] = D \]  

(24A)

(25A)

(26A)

The angle \( \Delta \) will be defined in such a way that the XY term (Eq. (25B)) equals to zero.

\[ B[\cos^2 (\Delta) - \sin^2 (\Delta)] - 2(A - C) \cos (\Delta) \sin (\Delta) = 0 \]  

(27A)

\[ B[\cos^2 (\Delta) - \sin^2 (\Delta)] = 2(A - C) \cos (\Delta) \sin (\Delta) \]  

(28A)

\[ B[\cos (2\Delta)] = 2(A - C) \sin (2\Delta) \]  

(29A)

\[ \tan (2\Delta) = B/(A - C) \]  

(30A)
Using Eq. (13A) and substituting the values of A, B, and C into Eq. (30A), one obtains the angle of rotation needed to make the XY term go to zero.

\[\tan(2\Delta) = -\frac{2\cos \phi}{(\text{exp}[-x]-\text{exp}[x])} = -\frac{2\cos \phi}{2 \sinh[x]} = -\frac{\cos \phi}{\sinh[x]} \] (31A)

With XY going to zero one can rewrite Eqs. (24A–26A) as

\[X^2[A \cos^2(\Delta) + B \cos(\Delta) \sin(\Delta) + C \sin^2(\Delta)] +
Y^2[A \sin^2(\Delta) - B \cos(\Delta) \sin(\Delta) + C \cos^2(\Delta)] = A'X^2 + C'Y^2 = D \tag{32A}\]

which can be written in the canonical ellipse form

\[
\frac{X^2}{(D/A')} + \frac{Y^2}{(D/C')} = 1
\] (33A)

So, to determine the semimajor and semiminor axes one needs to evaluate D/A' and D/C', respectively.

To evaluate these terms one first needs to evaluate the trigonometric functions in Eq. (32A). From Eq. (31A)

\[2\Delta = \arctan \left[-\frac{\cos \phi}{\sinh[x]}\right] \] (34A)

so

\[
\sin[2\Delta] = \sin \left[ \arctan \left[-\frac{\cos \phi}{\sinh[x]}\right] \right] = \frac{\cos \phi}{\sqrt{1 + \frac{\cos^2 \phi}{\sinh^2[x]}}} = \frac{\cos \phi}{\sqrt{\sinh^2[x] + \cos^2 \phi}} \] (35A)

but \(\sinh^2[x] = \cosh^2[x] - 1\) and \(\cos^2 \phi = 1 - \sin^2 \phi\) so Eq. (35B) becomes
\[
\sin[2\Delta] = \frac{\cos \varphi}{\sqrt{\cosh^2[x] - 1 + \sin^2 \varphi}} = \frac{\cos \varphi}{\sqrt{\cosh^2[x] - \sin^2 \varphi}} = \frac{\cos \varphi}{\sqrt{\alpha}} = 2\sin \Delta \cos \Delta \quad (36A)
\]

where \(\alpha = \cosh^2[x] - \sin^2 \varphi\) for convenience.

One also needs to determine \(\cos[2\Delta]\) and the square of \(\sin[\Delta]\) and the square of \(\cos[\Delta]\).

\[
\cos[2\Delta] = \cos \left[ \arctan \left( -\frac{\cos \varphi}{\sinh [x]} \right) \right] = \frac{-1}{\sqrt{1 + \frac{\cos^2 \varphi}{\sinh^2 [x]}}}
\]

\[
\cos[2\Delta] = \frac{-\sinh [x]}{\sqrt{\cosh^2[x] - 1 + \sin^2 \varphi}} = \frac{-\sinh [x]}{\sqrt{\cosh^2[x] - \sin^2 \varphi}} = -\frac{\sinh [x]}{\sqrt{\alpha}} \quad (37A)
\]

\[
\sin^2[\Delta] = \frac{1 - \cos[2\Delta]}{2} = \frac{1 + \frac{\sinh [x]}{\sqrt{\alpha}}}{2} = \frac{\sqrt{\alpha} + \sinh [x]}{2\sqrt{\alpha}} \quad (39A)
\]

\[
\cos^2[\Delta] = \frac{1 + \cos[2\Delta]}{2} = \frac{1 - \frac{\sinh [x]}{\sqrt{\alpha}}}{2} = \frac{\sqrt{\alpha} - \sinh [x]}{2\sqrt{\alpha}} \quad (40A)
\]

Substituting Eqs. (36A), (39A), and (40A) into A’ in Eq. (32A) gives

\[
X^2 \left[ \exp[x] \left( \frac{\sqrt{\alpha} - \sinh [x]}{2\sqrt{\alpha}} \right) - 2\cos \varphi \left( \frac{\cos \varphi}{\sqrt{\alpha}} \right) + \exp[-x] \left( \frac{\sqrt{\alpha} + \sinh [x]}{2\sqrt{\alpha}} \right) \right] \quad (41A)
\]

\[
X^2 \left[ \sqrt{\alpha} (\exp[x] + \exp[-x]) \frac{1}{2\sqrt{\alpha}} + \frac{(-\exp[x] + \exp[-x]) \sinh [x]}{2\sqrt{\alpha}} - \left( \frac{\cos^2 \varphi}{\sqrt{\alpha}} \right) \right] \quad (42A)
\]

\[
X^2 \left[ \cosh [x] + \frac{-\sinh^2 [x]}{\sqrt{\alpha}} - \left( \frac{\cos^2 \varphi}{\sqrt{\alpha}} \right) \right] \quad (43A)
\]

\[
X^2 \left[ \cosh [x] + \frac{-\sinh^2 [x] + \cos^2 \varphi}{\sqrt{\alpha}} \right] \quad (44A)
\]
Substituting Eq. (36A, 39A, 40A) into C’ in Eq. (32A) gives

\[ Y^2 \left[ \exp(x) \left( \frac{\sqrt{\alpha} + \sinh |x|}{2\sqrt{\alpha}} \right) + 2 \cos \phi \left( \frac{\cos \phi}{\sqrt{\alpha}} \right) + \exp[-x] \left( \frac{\sqrt{\alpha} - \sinh |x|}{2\sqrt{\alpha}} \right) \right] \] (47A)

\[ Y^2 \left[ \frac{\sqrt{\alpha} \exp(x) + \exp[-x]}{2\sqrt{\alpha}} + \frac{(\exp(x) - \exp[-x]) \sinh |x|}{2\sqrt{\alpha}} + \left( \frac{\cos^2 \phi}{\sqrt{\alpha}} \right) \right] \] (48A)

\[ Y^2 \left[ \cosh |x| + \frac{\sinh^2 |x|}{\sqrt{\alpha}} + \left( \frac{\cos^2 \phi}{\sqrt{\alpha}} \right) \right] \] (49A)

\[ Y^2 \left[ \cosh |x| + \left( \frac{\sinh^2 |x| + \cos^2 \phi}{\sqrt{\alpha}} \right) \right] \] (50A)

\[ Y^2 \left[ \cosh |x| + \frac{(\cosh^2 |x| - 1 + 1 - \sin^2 \phi)}{\sqrt{\alpha}} \right] = X^2 \left[ \cosh |x| + \frac{\alpha}{\sqrt{\alpha}} \right] \] (51A)

\[ Y^2 \left[ \cosh |x| + \sqrt{\alpha} \right] = C'Y^2 \] (52A)

By knowing A' and C' along with D one can determine the semimajor axis

\[ \frac{D}{A'} = \left( \frac{1}{2} \right) \exp[-(h_1 + h_2)] \sin^2 \phi \times \frac{\cosh |x| + \sqrt{\alpha}}{\cosh |x| + \sqrt{\alpha}} \] (53A)

\[ \frac{D}{A'} = \left( \frac{1}{2} \right) \exp[-(h_1 + h_2)] \] \[ \left[ \cosh |h_1 - h_2| + \sqrt{\cosh^2 |h_1 - h_2| - \sin^2 \phi} \right] \] (54A)
and the semiminor axis

\[
\frac{D}{C'} = \left(\frac{1}{2}\right) \exp\left[-(h_1 + h_2)\right] \sin^2\varphi \frac{\cosh [x] - \sqrt{\alpha}}{\cosh [x] + \sqrt{\alpha}} = \\
\left(\frac{1}{2}\right) \exp\left[-(h_1 + h_2)\right] \frac{\sin^2\varphi [\cosh [x] - \sqrt{\alpha}]}{\cosh^2 [x] - (\cosh^2 [x] - \sin^2 \varphi)}
\]

(55A)

\[
\frac{D}{C'} = \left(\frac{1}{2}\right) \exp[-(h_1 + h_2)]
\]

\[
[cosh \ [h_1 - h_2] - \sqrt{cosh^2 [h_1 - h_2] - \sin^2 \varphi}]
\]

(56A)

where one substitutes back in what \(x\) and \(\alpha\) are.

The semimajor and semiminor axis correspond to the maximum and minimum intensity of the elliptically polarized light observed through the analyzer.

\[
I_{max} = \left(\frac{1}{2}\right) \exp[-(h_1 + h_2)]
\]

\[
[cosh \ [h_1 - h_2] + \sqrt{cosh^2 [h_1 - h_2] - \sin^2 \varphi}]
\]

(57A)

\[
I_{min} = \left(\frac{1}{2}\right) \exp[-(h_1 + h_2)]
\]

\[
[cosh \ [h_1 - h_2] - \sqrt{cosh^2 [h_1 - h_2] - \sin^2 \varphi}]
\]

(58A)

The ratio of \(I_{min}/I_{max}\) is

\[
\frac{I_{min}}{I_{max}} = \frac{[cosh \ [h_1 - h_2] - \sqrt{cosh^2 [h_1 - h_2] - \sin^2 \varphi}]}{[cosh \ [h_1 - h_2] + \sqrt{cosh^2 [h_1 - h_2] - \sin^2 \varphi}]}
\]
\[
\frac{l_{\text{min}}}{l_{\text{max}}} = \frac{\cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}{\cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}
\]

(60A)

\[
\frac{l_{\text{min}}}{l_{\text{max}}} = \frac{\cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}{\sin^2 \varphi}
\]

(61A)

Likewise \(\frac{l_{\text{max}}}{l_{\text{min}}}\) is

\[
\frac{l_{\text{min}}}{l_{\text{max}}} = \frac{\cosh [h_1 - h_2] + \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}{\cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}
\]

(62A)

\[
\frac{l_{\text{min}}}{l_{\text{max}}} = \frac{\cosh [h_1 - h_2] + \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}^2}{\cosh^2 [h_1 - h_2] - \cosh^2 [h_1 - h_2] + \sin^2 \varphi}
\]

(63A)

\[
\frac{l_{\text{min}}}{l_{\text{max}}} = \frac{\cosh [h_1 - h_2] + \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}^2}{\sin^2 \varphi}
\]

(64A)

By adding the square root of Eqs. (61A) and (64A) one obtains

\[
\sqrt{\frac{l_{\text{min}}}{l_{\text{max}}}} + \sqrt{\frac{l_{\text{min}}}{l_{\text{max}}}} = \frac{\cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi} + \cosh [h_1 - h_2] - \sqrt{\cosh^2 [h_1 - h_2] - \sin^2 \varphi}}{\sin \varphi}
\]

(65A)

\[
\sqrt{\frac{l_{\text{min}}}{l_{\text{max}}}} + \sqrt{\frac{l_{\text{min}}}{l_{\text{max}}}} = \frac{2 \cosh [h_1 - h_2]}{\sin \varphi}
\]

(66A)
Where solving for \( \sin \varphi \) one obtains the relationship used to determine the retardation of the light coming from the analyzer to the photodetector.

\[
\sin \varphi = \frac{2 \cosh [h_1 - h_2]}{\sqrt{l_{\min}/l_{\max}} + \sqrt{l_{\max}/l_{\min}}} \cdot \sqrt{l_{\min}/l_{\max}}
\]  
\( \text{(67A)} \)

\[
\sin \varphi = \frac{2 \sqrt{l_{\min}/l_{\max}} \cosh [h_1 - h_2]}{1 + l_{\min}/l_{\max}}
\]  
\( \text{(68A)} \)
APPENDIX B
MICELLANEOUS DATA

Figure 1B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid using a parallel-plate fixture at $H = 100$ Oe.
Figure 2B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid with parallel-plate fixture at $H = 250$ Oe.

Figure 3B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid with parallel-plate fixture at $H = 500$ Oe.
Figure 4B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid with cone-and-plate fixture at $H = 0$ Oe.

Figure 5B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid with cone-and-plate fixture at $H = 100$ Oe.
Figure 6B Plots of $\sigma$ versus $\dot{\gamma}$ for 24% MR fluid using a cone-and-plate fixture at $H = 250$ Oe.

Figure 7B Plots of $\sigma$ versus $\dot{\gamma}$ for 40% MR fluid using a cone-and-plate fixture at $H = 0$ Oe.
**Figure 8B** Plots of $\sigma$ versus $\dot{\gamma}$ for 40% MR fluid using a cone-and-plate fixture at $H = 100$ Oe.

**Figure 9B** Plots of $\sigma$ versus $\dot{\gamma}$ for 40% MR fluid using a cone-and-plate fixture at $H = 250$ Oe.
Figure 10B Plots of $\sigma$ versus $\dot{\gamma}$ for 40% MR fluid using a cone-and-plate fixture at $H = 500$ Oe.

Figure 11B Plots of $\sigma$ versus $\dot{\gamma}$ for 30% MR fluid using a cone-and-plate fixture at $H = 0$ Oe.
Figure 12B Plots of $\sigma$ versus $\dot{\gamma}$ for 30% MR fluid using a cone-and-plate fixture at $H = 250$ Oe.

Figure 13B Plots of $\sigma$ versus $\dot{\gamma}$ for 30% MR fluid using a cone-and-plate fixture at $H = 750$ Oe.
Figure 14B Plots of $\eta$ versus $\dot{\gamma}$ for 24% MR fluid at $H = 250$ Oe.

Figure 15B Plots of $\eta$ versus $\dot{\gamma}$ for 40% MR fluid at $H = 0$ Oe.
Figure 16B Plots of $\eta$ versus $\dot{\gamma}$ for 40% MR fluid at $H = 100$ Oe.

Figure 17B Plots of $\eta$ versus $\dot{\gamma}$ for 40% MR fluid at $H = 250$ Oe.
Figure 18B Plots of $\eta$ versus $\dot{\gamma}$ for 40% MR fluid at $H = 500$ Oe.

Figure 19B Plots of $\eta$ versus $\dot{\gamma}$ for 30% MR fluid at $H = 0$ Oe.
Figure 20B Plots of $\eta$ versus $\dot{\gamma}$ for 30% MR fluid at $H = 250$ Oe.

Figure 21B Plots of $\eta$ versus $\dot{\gamma}$ for 30% MR fluid at $H = 750$ Oe.
Figure 22B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-VI at $H = 500$ Oe.

Figure 23B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-III at $H = 0$ Oe.
Figure 24B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-III at $H = 500$ Oe.

Figure 25B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-V at $H = 0$ Oe.
**Figure 26B** Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-V at $H = 500$ Oe.

**Figure 27B** Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-V at $H = 1000$ Oe.
Figure 28B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-II at $H = 0$ Oe.

Figure 29B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-II at $H = 500$ Oe.
Figure 30B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 900-II at $H = 1000$ Oe.

Figure 31B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900-III at $H = 0$ Oe.
Figure 32B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900-V at $H = 0$ Oe.

Figure 33B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 900-II at $H = 0$ Oe.
Figure 34B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 905 at $H = 100$ Oe.

Figure 35B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 905 at $H = 250$ Oe.
Figure 36B Plots of $\sigma$ versus $\dot{\gamma}$ for EMG 905 at $H = 350$ Oe.

Figure 37B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 0$ Oe.
Figure 38B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 100$ Oe.

Figure 39B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 250$ Oe.
Figure 40B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 350$ Oe.

Figure 41B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 500$ Oe.
Figure 42B Plots of $\sigma$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 1420$ Oe.

Figure 43B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 905 at $H = 0$ Oe.
Figure 44B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 905 at $H = 100$ Oe.

Figure 45B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 905 at $H = 250$ Oe.
Figure 46B Plots of $\eta$ versus $\dot{\gamma}$ for EMG 905 at $H = 350$ Oe.

Figure 47B Plots of $\eta$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 0$ Oe.
Figure 48B Plots of \( \eta \) versus \( \dot{\gamma} \) for filtered EMG 905 at \( H = 100 \) Oe.

Figure 49B Plots of \( \eta \) versus \( \dot{\gamma} \) for filtered EMG 905 at \( H = 250 \) Oe.
Figure 50B Plots of $\eta$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 350$ Oe.

Figure 51B Plots of $\eta$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 500$ Oe.
Figure 52B Plots of $\eta$ versus $\dot{\gamma}$ for filtered EMG 905 at $H = 1420$ Oe.