The Varied Thermal Response of Magnetic Iron-Oxide Nanoparticles During Induction Heating in Liquid and Solid-Liquid Phase Change Mediums

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The Varied Thermal Response of Magnetic Iron-Oxide Nanoparticles During Induction Heating in Liquid and Solid-Liquid Phase Change Mediums

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Of the requirements for the degree of
Master of Science in Mechanical Engineering

by

Joshua Tompkins
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This thesis is approved for recommendation to the Graduate Council.

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ABSTRACT

This study investigates the induction heating response of uncapped iron oxide nanoparticles sonically dispersed as a nanofluid and mechanically distributed in solid phase change materials. The nanoparticles examined have a mean diameter of 14.42 nm and are magnetically heated in an alternating magnetic field at an amplitude of 72.6 kA/m at frequencies of 217, 303, and 397 kHz. Nanoparticle characterization was undertaken through transition electron microscopy, x-ray diffraction, and dynamic light scattering when in suspension. Carrier fluids were characterized through viscosity, heat capacity, and density measurements which were used in the calorimetric calculation of the specific absorption rate (SAR) of the samples which is based on the nanoparticle concentration, carrier medium heat capacity, and the time-temperature response. The SAR of these samples is compared based on nanoparticle concentration, field frequency, and carrier medium viscosity. All samples types demonstrate SAR reductions with increasing nanoparticle concentration and SAR enhancement with increasing frequency. Nanofluid samples demonstrate a peak SAR value at the lowest viscosity examined, 1.024 mPa.s, with SAR attenuation with increasing viscosity up to 17.12 mPa.s. However, samples ranging from 171.6 to 234 mPa.s saw little variation with viscosity denoting the inhibition of Brownian relaxation in these samples. Dynamic light scattering of the nanofluids illustrates nanoparticle clustering which corresponds to viscosity potentially muddying the effective contributions of Brownian relaxation. Nanoparticles embedded in a solid PCMs of Paraffin wax and D-Sorbitol were investigated to reasonably characterize the SAR output of Néel relaxation dominated heating. The SAR results of the two PCM mediums correspond well at each concentration and field frequency demonstrating the Néel contribution to heating and the reasonable assumption of inhibited Brownian relaxation. Comparisons of SAR between solid
embedded PCM samples and highly viscous nanofluids confirms Brownian inhibition at high viscosity for these nanoparticles. Analysis of the onset of Brownian relaxation during heating with a solid to liquid phase change sees an approximately 15.6% increase in the SAR of the low viscosity liquid Paraffin with a 10% decrease in SAR noted for the extremely viscous liquid D-Sorbitol. This result is attributed to the disparate liquid environments where nanoparticle settling is pronounced at low viscosity in Paraffin. Discussion on the precise contribution to SAR of Brownian relaxation is presented based on a limited set of data with consideration given to variations in SAR of the PCM samples for solid versus liquid states of heating. This study encompasses a wide range of carrier mediums and provides a thorough analysis of the heating response of iron oxide nanoparticles with focus on the Brownian contribution to heating.
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DEDICATION

This work is dedicated to the love of my life, Momo. You have taught me more in our short time together than any paper, course, or devastating failure ever could. Thank you for your continued support and affection. I love you dearly.
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CHAPTER 1 Introduction

The widespread research into the field of nanomaterials spanning the past few decades has illuminated the myriad properties and potential application areas of nanoparticles. One widely investigated aspect of this body of research involves the thermal response of Magnetic Nanoparticles (MNP) dispersed in a liquid carrier medium exposed to induction heating in an Alternating Magnetic Field (AMF). Suspensions and colloids of MNP have been investigated for their projected value in locally treating tumors in a process called magnetic hyperthermia. The procedure for which requires the injection of MNFs into the tumor followed by exposure of the injection site to an AMF thereby locally heating the malignant cells. Research has shown that tumor cells will die at temperatures above 42 °C [1, 2] due to ruptures in the cell walls. Medical intervention of this type has the potential to treat the disease while causing less damage to the surrounding cells of the patient compared to traditional therapies. However, targeted applications such as magnetic hyperthermia require a fundamental understanding of the underlying factors influencing the thermal output of a MNF during induction heating. The basis of this field of research builds upon a 2002 paper by R. E. Rosensweig which details the underlying theory and computations for power loss, in the form of thermal energy, of ferrofluids in an AMF [3]. The principle factors affecting power loss of a monodisperse ferrofluid as described by Rosensweig are presented in Equation 1.

\[
P = \pi \mu_0 \chi_0 H_0^2 f \left( \frac{2\pi f \tau}{1 + (2\pi f \tau)^2} \right)
\]

Here, \(P\) is the volumetric power loss of the MNF, \(\mu_0\) is the permeability of free space, \(\chi_0\) is the magnetic susceptibility of the nanoparticles, \(H_0\) is the peak magnetic field strength, \(\tau\) is the effect
relaxation time constant, and f is the AMF frequency. The variables in Equation 1 denote the importance of AMF field strength and frequency, the magnetic properties of the nanoparticles, and the effective relaxation of the nanoparticles. The AMF field strength and frequency are dictated by the experimental setup through the induction heater’s capacitance, coil geometry, and applied current [4]. Additionally, as Rosensweig describes, the magnetic susceptibility of the nanoparticles depends on the AMF strength as well as the nanoparticle’s magnetic volume, domain magnetization, volume fraction of solids, and temperature. Lastly, the effective relaxation of the nanoparticles considers the two principle aspects through which heating occurs in an MNF: the physical interaction of the nanoparticle and the carrier medium – Brownian relaxation, and the intraparticle magnetic moment interaction with the magnetic field – Néel relaxation [3, 5]. In a MNF these mechanisms contribute to heating simultaneously with varying degrees of contribution depending on the properties of the MNP and the environment of the carrier medium. The combined effective relaxation, $\tau$, is given by the following equation.

$$\frac{1}{\tau} = \left(\frac{1}{\tau_B}\right) + \left(\frac{1}{\tau_N}\right)$$

(2)

In a simplified sense, Brownian relaxation concerns the rotation of the nanoparticle in the carrier fluid providing heat through drag on the particle. In contrast, Néel relaxation induces heating through the continual realignment of the magnetic domain with the AMF. These time constants are calculable through the following equations:

$$\tau_B = \frac{(3\mu V_H)}{(k_B T)}$$

(3)
\[ \tau_N = \tau_0 \exp \left[ \frac{(K_a V_M)}{(k_B T)} \right] \]  

(4)

where \( \tau_B \) is Brownian relaxation expressed in seconds, \( \mu \) is the viscosity of the carrier fluid, \( V_H \) is the hydrodynamic volume, \( k_B \) is Boltzmann's constant, \( T \) is the absolute temperature in Kelvin, \( \tau_0 \) is a time constant (typically presented as \( 10^{-9} \) seconds), \( \tau_N \) is the Néel relaxation expressed in seconds, \( K_a \) is the anisotropy constant of the nanoparticles, \( V_M \) is the magnetic volume, and \( \tau \) is the effective relaxation time [3, 6, 7]. Equations 3 and 4 highlight and contrast the main factors affecting heating for Brownian and Néel relaxation. The former relaxation mode concerns the viscosity of the carrier medium and the hydrodynamic volume of the particles which may include the magnetic volume, the iron-oxide particle core, and any capping agent which may be functionalized to the particle’s surface, while, in contrast, Néel relaxation is dependent upon the anisotropy of the nanoparticles and only the magnetic volume of the nanoparticles. The general method of characterizing the heat output of a nanofluid is through the calorimetric calculation of the specific absorption rate (SAR), also commonly referred to as the specific loss power, which is a measure of thermal output on a per mass basis. The calculation of SAR is provided below in Equation 5.

\[ \text{SAR} = \left( \frac{C_p}{\varphi} \right) \left( \frac{dT}{dt} \right) \]  

(5)

Where \( C_p \) is the specific heat capacity of the carrier medium, \( \varphi \) is the mass fraction of nanoparticles in the sample, and \( dT/dt \) is the initial temperature rise of the sample. The calculation of mass fraction is merely the ratio of the mass of nanoparticles to the mass of the system as a whole and is provided in Equation 6.
Herein, \( m_{NP} \) is the mass of the nanoparticles in the sample and \( m_{CM} \) is the mass of the carrier medium whether solid or liquid. A review of the pertinent literature will explore the multitude of major factors influencing the overall heating output such as the effects of AMF frequency, nanoparticle concentration, and carrier medium viscosity. Within the umbrella of these principle factors, additional discussion will consider variables influencing the heating response such as nanoparticle diameter, the strength of the AMF, and nanoparticle surface chemistry.

**1.1 AMF Frequency and Amplitude Effects on the Heating Output of Magnetic Nanofluids**

The effects of AMF frequency on the heating output of nanofluid suspensions have been investigated through simulation and the calorimetric calculation of SAR. General trends in the effects of SAR are apparent with mild variation depending upon the various factors of the induction heating system. A 2009 study by Kim et al. investigated the SAR of spinel MnFe\(_2\)O\(_4\) nanoparticles with diameters of 5.3, 7.4, 10.5, and 12.1 nm dispersed in water, and these samples were exposed to an AMF at 231 and 266 kHz and at field strengths of 131, 261, 392, 522, and 653 Oe [2]. For most field amplitudes, each sample type signified an increase in SAR when exposed to a higher frequency. The authors further examined the SAR of the 10.5 nm sample, which demonstrated the greatest SAR of any sample across the board and demonstrated linear enhancements with frequency for field strengths of 150, 200, and 250 Oe. Similarly, a 2015 study by Smolkova et al. investigated the SAR of 13 nm iron oxide NP dispersed in glycerol in varying concentrations [8]. Samples exposed to a magnetic field amplitude of 5.8 kA/m at frequencies of 525 and 1048 kHz demonstrated increases in SAR for all sample concentrations.
and particle treatments. Although, the limited sampling of fixed field amplitudes with varied AMF frequencies does not allow for the assertion of linear enhancement in this study. Usov and Liubimov further illuminate the effects of AMF frequency in their 2012 paper which considers the pairing of field frequency and amplitude for dilute assemblies of uniaxial MNPs in water [9]. This study considers field amplitude, $H_0$, in comparison to the nanoparticle anisotropy field, $H_k$, demonstrating a heating response dependent upon the proportionality of these two values. The authors consider two modes of heating: the viscous mode, $H_0 << H_k$, and the magnetic mode where $H_0 \geq 0.5H_k$. Comparison of SAR for 40 nm MNP with an $H_k$ value of 500 Oe are compared across several frequencies and field amplitudes. In the viscous mode, the heating output is largely insensitive to frequency with a field amplitude of 100 Oe seeing, essentially, no enhancement with SAR for AMF frequencies spanning 100 to 600 kHz. At a field amplitude of 200 Oe, there is an approximately 60 percent increase in SAR from 100 kHz to 500 kHz; however, the greatest increase in heating occurs from 100 to 200 kHz with a reduced increase in SAR with each 100 kHz step increase. At a field strength of 250 Oe, equivalent to $0.5H_k$, there is a strongly linear enhancement of SAR for all frequencies in the range examined. Further comparison of SAR for frequencies of 100 and 500 kHz at field strengths ranging 100 to 300 Oe demonstrates that a higher field frequency mildly enhances SAR at field amplitudes in the viscous mode, with the transition into the magnetic mode denoting a far more impressive increase in SAR. The key takeaway from this paper is the pairing of field frequency and amplitude which, depending on the magnetic properties of the nanoparticles utilized, will see varying degrees of SAR enhancement. For a field strength less than half of the anisotropy field of the nanoparticles the SAR enhancement is mild at best, but around $H_0 = 0.5H_k$ this enhancement takes on a linear form with increasing frequency. A 2019 paper by Yoshida et al.
investigated the effects of AMF frequency and amplitude on mixtures of water and glycerol with discrete viscosities of 0.957, 9.43, and 411 mPa.s, with samples dubbed S1, S2, and S3, respectively [10]. Resovist nanoparticles were utilized with an average core size of 27.5 nm, and a hydrodynamic diameter of 60.5 nm in concentrations of 1 mg/ml. These samples were evaluated through M-H curves at 3 and 20 kHz frequencies in 3.5 and 20 mT field amplitudes resulting in four distinct data sets. At a field amplitude of 3.5 mT and a frequency of 3 kHz, sample S1 demonstrated the greatest hysteresis area at 0.274 J/kg-Fe with sample S2 and S3 considerably smaller with values of 0.152 and 0.117 J/kg-Fe, respectively. Increasing the frequency to 20 kHz showed attenuation in the hysteresis area of all samples with S1 dropping to 0.156 J/kg-Fe with samples S2 and S3 demonstrating nearly identical values of 0.155 and 0.144 J/kg-Fe, respectively. Raising the field amplitude of 20 mT further demonstrates the insensitivity to viscosity of these samples with nearly identical hysteresis areas for all samples with values ranging 1.28 – 1.40 J/kg-Fe at 3 kHz, and 2.00 – 2.06 J/kg-Fe at 20 kHz. These results indicate hysteresis losses are dependent on viscosity only at low field frequency and amplitudes, with higher amplitude fields resulting in a consistent hysteresis area, independent of viscosity, which enhances with frequency. The authors go on to discuss the ideal power loss scenario where the AMF frequency is greater than the field dependent Brownian relaxation frequency, but less than the field dependent Néel relaxation frequency indicating a reasonable application area for magnetic hyperthermia applications. A more recent study by Usov et al. considers the frequency effects of nanoparticle clusters characterized through an author defined value of their filling factor [11]. The filling factor is the ratio of the product of the number of nanoparticles in a cluster and their mean volume over the, assumed, spherical volume of the entire cluster. Clusters with filling factors of 0.04, 0.18, and 0.32 were considered in calculations with mean
nanoparticle diameters of 20 nm for an AC field with an amplitude of 100 Oe at frequencies spanning 200 to 750 kHz. The presented data shows a linear enhancement of SAR with frequency for all three clusters with the slope of the enhancement inversely proportional to the filling factor. Considering nanoparticle diameter with respect to SAR for a filling factor of 0.18 demonstrates the variance in heating with respect to field amplitude at 400 kHz. The data presented shows increasing SAR with higher field strength, with SAR maxima occurring at 21 nm for a 150 Oe field and 20 nm for 100 and 50 Oe fields. The same general trend of SAR increasing with diameter up to a peak and decreasing above this diameter threshold is evident in all field strengths with varying degrees of presentation. This data seems to indicate that nanoparticle clustering presents similar trends of enhancement with AMF frequency and amplitude which presents itself in differing ways depending on the degree of clustering and the AMF utilized.

1.2 Nanoparticle Diameter, Concentration, and Clustering Effects on Heating Output

Many studies have investigated the effects of nanoparticle size, concentration, and aggregation on the heating output of nanofluids with differing results consistently reported across the body of literature. Returning to the 2009 study by Kim et al. [2] provides evidence of diameter specific SAR maximization. Nanoparticles with a diameter of 10.5 nm exhibited the greatest SAR for most field strengths at both AMF frequencies while the 5.3 nm particles demonstrated the lowest SAR across all field strengths for both frequencies. In general, SAR increased with particle size maximizing at 10.5 nm before seeing a reduction in heating output at 12.1 nm for most field strengths and for both frequencies. This variance in SAR with nanoparticle size is attributed to differences in the dominating relaxation mode of the
nanoparticles which is governed by the shorter relaxation. The authors calculated and plotted the theoretical Brownian and Néel relaxation of these MNF with respect to particle diameter demonstrating the shift in effective relaxation from one dominated by Néel relaxation for diameters below 10 nm to Brownian domination above this threshold. Considering Equation 1 and noting that the theoretical maximum thermal dissipation occurs when $2\pi f\tau = 1$, allows for the calculation of a nanoparticle size which maximizes the heat output for a particular field frequency. Kim et al. examined frequencies from 165 to 266 kHz which correspond maximized heating for nanoparticles of diameters spanning from 9.8 to 10.3 nm, and these estimates closely relate to the observed experimental trends which saw SAR peak for particles of 10.5 nm. Building upon these findings, Bakoglidis et al. investigated the SAR of iron oxide nanoparticles spanning a range of 5 to 18 nm in varying concentrations with discussion on the principle contributions to heating for distinct particle size ranges in an AMF with a field frequency of 765 kHz and an amplitude of 20 kA/m [12]. The authors divide the particles into three categories where diameters up to 10 nm considered superparamagnetic with Néel relaxation dominating heating, an intermediate superparamagnetic and ferromagnetic transition region from 10 to 13 nm, and a ferromagnetic region with hysteresis losses contributing the most to heating for particles above 13 nm. At a concentration of 0.3 mg/ml, SAR increased with particle size up to a local maximum at 10 nm that the authors attribute to the critical diameter where Néel relaxation is maximized. At 13 nm SAR has decreased significantly, but for diameters above this range, where hysteresis losses dominate, SAR increases rapidly to an overall maximum at 18 nm. Comparison of the effects of concentration for 10 and 18 nm particles illuminate the differences in the impact on SAR for these particles. The 18 nm particles demonstrate a reasonably consistent decrease in SAR going from 0.15 to 1.2 mg/ml which the authors attribute to dipolar
interactions enhancing stability against the AMF. Conversely, 10 nm particles increase in SAR from 0.15 to 0.3 mg/ml where they maximize, followed by a significant reduction in SAR which is relatively consistent at 0.6, 0.9, and 1.2 mg/ml; indicating that concentration also affects nanoparticles in a Néel relaxation dominated system where they maximize heating at a concentration specific to the AMF. The size of the nanoparticles seems to indicate the magnetic mode of heating experienced with larger diameter particles seeing a reasonably high level of heating owed to hysteresis losses.

In consideration of nanoparticle concentration, a 2010 study by Urtizberea et al. investigated non-agglomerated and monodispersed maghemite nanoparticles with a mean diameter of 11.6 nm [13]. These MNF samples were exposed to a 3 kA/m AMF amplitude at 109 kHz at concentrations of 8.14, 4.65, and 1.89 mg/ml and the resulting SAR of these samples was 0.38, 0.47, and 0.89 W/g, respectively. This trend of SAR attenuation with nanoparticle concentration enhancement is ascribed to dipolar interactions between particles. The authors discuss the possible outcomes of interparticle dipolar interactions as decreasing the static susceptibility of the NP thereby stabilizing them against the AMF, and as decreasing the relaxation time thereby providing heating enhancement at a lower frequency. The latter assertion is further supported by calculating the optimum frequency for each concentration by assuming $2\pi f\tau = 1$ which demonstrates optimum excitation frequencies that decrease with increasing concentration, thereby necessarily enhancing SAR for lower concentrations which maximize closer to the applied AMF frequency of 109 kHz. Conversely, Smolkova et al. investigated concentrations of 2, 5, and 7 wt% of 13 nm magnetite nanoparticle dispersed in glycerol and demonstrated increases in SAR with increasing concentration [8]. This finding held true for all
AC field frequencies and amplitudes and for nanoparticles which were annealed for 2 and 6 hours to transition the magnetite into maghemite; however, annealing the particles demonstrated no significant changes in SAR over the original sample. The findings of this study were also attributed to interparticle interactions which the authors say increases the effective magnetic anisotropy thereby reducing the impacts of thermal fluctuations on magnetization of the particles. A 2011 study by Piñeiro-Redondo et al. further muddies the water of concentration effects by reporting opposite effects with concentration for 9 nm uncapped and polyacrylic acid (PAA) capped magnetite nanoparticles [1]. For an AC field of 15 mT at 308 kHz, concentrations spanning 0.6 to 20 mg/ml demonstrated consistent reductions in SAR for PAA capped nanoparticles with uncapped nanoparticles increasing in SAR with from 0.6 to 10 mg/ml. Reduction of SAR for PAA capped particles is attributed to interparticle dipole interactions, the usual culprit, while the authors attribute aggregation phenomena to the enhancement of uncapped particles, but they note further research is required to fully understand the problem. Up to this point, studies have indicated conflicting information regarding the coupling of SAR and nanoparticle concentration in MNFs. However, a 2014 review by Deatsch and Evans provides an overview of the existing research up to their publication and helps to elucidate the reported trends [14]. Their review catalogs five studies which conclude SAR attenuation with concentration, two which demonstrate no changes in SAR, and four studies stating SAR increases with concentration. Deatsch and Evans buck the assertion that research is contradictory or conflicting in regard to concentration effects and state that the existing body of research indicates that increasing particle concentration decreases relaxation time up to, but excluding, the onset of particle aggregation at sufficiently high concentrations, thereby ascribing SAR enhancement with concentration.
An early effort which highlighted the potential effects of nanoparticle clustering comes from a 2008 study by Dennis et al. which involved 92 nm dextran coated iron oxide nanoparticles which demonstrated SAR enhancement dependent upon the degree of particle aggregation [15]. In an AMF with a frequency of 150 kHz and an amplitude of 86 kA/m, samples with equivalent saturation magnetizations and concentrations demonstrated a seven-fold increase in SAR when “tightly associated” compared to a “loosely associated” sample. The variation in association is attributed to the thickness of the dextran layer with the tightly associated system receiving two coats. The authors attribute the smaller interparticle distance as enhancing dipolar interactions that couple the collective behavior of the nanoparticles. A 2018 study by Carlton et al. looks at the effects of concentration and carrier medium on the SAR output of TX-100 capped magnetite and maghemite particles with a mean diameter of 17.5 nm [16]. Solutions in concentrations of 5 and 10 mg/ml were made with nanoparticles dispersed in saline solutions with sodium chloride molarity varied between 0.0 and 0.9 M. This study demonstrated SAR reductions with increasing concentration attributed, again, to dipole-dipole interactions increasing the anisotropic energy barrier which inhibit relaxation mechanism. Interestingly, this study also considers the effects on nanoparticle aggregation as a function of saline molarity and reports a strong correlation between NaCl molarity and the effective hydrodynamic diameter of the nanoparticles in suspension. This finding, paired with the strong increase in SAR with increasing NaCl molarity, indicates that nanoparticle clustering may in fact lead to heating enhancement. Experimental work by Serantes et al. in 2014 considers lengths of magnetite nanoparticle chains and how they affect heating, with individual particles having a diameter of 44 nm [17]. A 300 Oe AC field alternating at 765 kHz was applied to chains of nanoparticles which were dispersed in 0.5 and 1 percent agar with the chain orientation to the magnetic field
considered. The SAR of both sample types demonstrated a maximum SAR when the chains aligned with the AMF at 0°, with SAR attenuation obvious at 45°, and a minimum SAR value observed when the chains were parallel to the AMF lines at 90°. Interestingly, the authors note that nanoparticle chains may have a specific length in which heating is maximized, which they estimate is around 8 nanoparticles in length, beyond which there is no additional enhancement with heating. Indeed, a 2015 study by Cabrera et al. presents a similar trend for 20 nm iron oxide nanoparticles dispersed in water and 5 % agar for a field amplitude of 50 mT at a frequency of 105 kHz [18]. A plot presenting SAR of a 5 % agar solution denotes SAR enhancement from an initial $D_H$ of approximately 50 nm up to a maximum at ~95 nm. Further aggregation demonstrates reductions in SAR as $D_H$ increases with a diameter of 140 nm comparable in heating output to a $D_H$ of 50 nm, and minimum SAR observed at 220 nm. This study also considers the effects of concentration on SAR with divergent results dependent upon the carrier medium: water based samples at 10mg/ml demonstrated SAR enhancement over a 3 mg/ml sample while 5 % agar solutions saw SAR attenuation at the higher concentration compared to the lower. The SAR trend with hydrodynamic diameter observed in the agar-based samples may help to explain the reductions in SAR with increasing concentration. For the experimental setup described, higher concentrations of nanoparticles would lead to reductions in the interparticle distance which could lead to pronounced aggregation thereby reducing the SAR of the sample. Similarly, SAR enhancement with concentration observed in the water-based samples could also be due to an increase in effective $D_H$ maximizing SAR which differs from the agar-based samples. Essentially, each MNF could present differing degrees of nanoparticle aggregation at each concentration level and could be the cause of the divergent SAR values, owing to different hydrodynamic diameters maximizing SAR in each sample. Moreover, the observed ~95 nm
hydrodynamic diameter which maximizes SAR should be specific to this AMF frequency, amplitude, and agar-based carrier medium and, while still helping to elucidate potential heating trends, is certainly not a broadly applicable observation. Depending on the study, interparticle dipole effects seemingly enhance or attenuate SAR with increasing concentration which broadly depends upon the nanoparticle’s diameter and degree of clustering. Hysteresis losses tend to occur with enhancements of interparticle dipole-dipole interactions which reduce the heating output, although some sources indicate an ideal level of nanoparticle clustering which leads to enhancement. The previously discussed 2019 study by Usov et al. further builds the idea of nanoparticle clustering and its relation to SAR through the investigation of distinct cluster sizes [11]. Nanoparticle clusters were investigated using nanoparticles with individual diameters ranging from 10 to 60 nm in clusters of 60 to 90 nanoparticles. These clusters were further characterized by their filling factor in discrete steps of 0.005, 0.04, 0.18, and 0.32 which is the ratio of the number of nanoparticles in the cluster times the volume of these nanoparticles to the volume of the clustered nanoparticles which are assumed to be spherical. These dilute assemblies of 3D nanoparticle clusters were examined in an AMF with an amplitude of 100 Oe at a frequency of 400 kHz. At filling factors of 0.005 and 0.04 SAR shows extreme enhancement with nanoparticle diameter maximizing around 21 nm, but then dropping off as the diameter continues to increase. Similar effects are noted at filling factors of 0.18 and 0.32, but the variance in SAR is less pronounced and the peak SAR value occurs at around 20 nm instead. Further expounding upon these findings, the authors investigate the SAR of clusters at filling factors of 0.0, 0.04, and 0.18 at 100 Oe and note SAR maximum dependent upon nanoparticle diameter with lower filling factors maximizing at larger particle diameters. The authors also present a trend in SAR which indicates relatively consistent SAR results independent of nanoparticle
diameter at a filling factor of 0.18. This result shows an increase in SAR starting at 15 nm which plateaus around 25 nm and relatively consistent thereafter, only showing some signs of attenuation above 50 nm in a limited section of data. This study helps to further underline the myriad factors influencing the heating output of MNF by characterizing SAR for discrete nanoparticle clusters which indicates an ideal particle sizes for a specific level of clustering which maximizes SAR. At first glance this study seems at odds with the findings of Dennis et al. [15] which presented SAR enhancement for a tightly associated system compared to a loosely associated one, however, the stark SAR maxima associated with a filling factors 0.005 and 0.04 is present only in a limited diameter range. Indeed, outside of this range, spanning approximately 16 to 24 nm, the SAR results of the higher filling factor samples, 0.18 and 0.32, demonstrate greater heating output. Specifically, at a diameter of 28 nm filling factors of 0.18 and 0.32 both outperform the less filling factors and present stark similarity in SAR. This level of SAR enhancement is far from the 7-fold enhancement seen in [15], but nonetheless demonstrates the wildly variable SAR output of clustered nanoparticles which shows dependency on not only nanoparticle diameter but also the AMF.

1.3 The Effects of Carrier Medium Viscosity on the Heating Output of Nanoparticles

Considering Equation 3 brings to light the effect of the carrier medium’s viscosity will have on the heating output of an MNF in an AMF: high viscosity should lead to reductions in heating. This is due to the increased time associated with Brownian relaxation which, in his 2002 paper, Rosensweig [3] indicated would prevent elevated heating rates for ferrofluids. The effects of viscosity have been investigated by multiple studies with the body of research in general consensus of the conclusions [1, 10, 18-22]. The previously discussed study by Cabrera et al.
looking at 20 nm iron oxide particles in water and 5% agar solutions demonstrated reductions in SAR between the two sample types [18]. Similarly, Suto et al., 2009, reported the response of 12.5 and 15.7 nm magnetite particles exposed to an AC field at 40 Oe and 600 kHz [21]. The authors considered a limited set of differently viscous mediums using water and hydrogel and observed a 27% decrease in SAR in hydrogel for the 12.5 nm particles, and a 67% increase with the 15.7 nm particles. Consideration of hysteresis losses in a viscous environment was investigated by Yoshida et al. with their findings demonstrating hysteresis attenuation with viscosity for mixtures of water and glycerol in three distinct viscosities of 0.954, 9.43, and 411 mPa.s [10]. However, this study notes that this is only valid at a field amplitude and frequency of 3.5 mT and 3 kHz and increasing the frequency to 20 kHz sees the variation in hysteresis area reduced. Indeed, at 20 mT and both 3 and 20 kHz frequencies the hysteresis area is entirely insensitive to viscosity. In 2007, Zhang et al. investigated 20 nm dextran coated magnetite particles using an AMF frequency of 55 kHz at an amplitude of 200 Oe [22]. Samples were tested in ferrofluid solutions with viscosities ranging from 1 to approximately 5.4 mPa.s. Increasing from a minimum value of 57 W/g at 1 mPa.s, SAR peaks at 76 W/g around 1.96 mPa.s before gradually decreasing with each increasing step in viscosity. This result is seemingly at odds with the theoretical calculation of Brownian relaxation; however, this trend is illuminated by other authors. Piñeiro-Redondo et al. investigated SAR and viscosity for PAA capped magnetite nanoparticles with a 10 nm diameter at 15 mT and 308 kHz [1]. These nanoparticles were dispersed in four distinct mediums: water, ethylene glycol, 1-2 propanediol, and PEG 400 with viscosities of 1, 17, 40.4, and 90 mPa.s, respectively. The SAR response at a concentration of 20 mg/ml was reported with comparable values of 36.5 and 37.3 W/g occurring at 1 and 17 mPa.s, respectively. The two higher viscosity samples demonstrated reductions in SAR with
increasing viscosity. This result is similar to [22] where SAR peaks at a certain viscosity before reducing as expected. Piñeiro-Redondo et al. discuss why this happens by considering the peak dissipation occurring at $2\pi f\tau = 1$ and developing an equation to calculate the viscosity at this value depending on the diameter of the nanoparticles in use. The authors calculate maximized SAR at approximately 22 mPa.s for their 10 nm particles which corresponds well to the observed SAR maxima at 17 mPa.s. Plotting viscosity against nanoparticle diameter demonstrates that as the diameter of the nanoparticles increases the viscosity which maximizes heating quickly reduces, and a 25 nm diameter particle demonstrates maximized heating at approximately 1 mPa.s. Fortin et al. discussed the SAR findings of magnetite and cobalt ferrite nanoparticle of varying size dispersed in water and mixtures of water and glycerol in an AMF with amplitude 24.8 kA/m at a frequency of 700 kHz [19]. Their results showed both a coupling of nanoparticle diameter with SAR, noting a peak heating performance around 10 nm, and viscosity and SAR. The latter of which marked incredible SAR attenuation with increasing viscosity for cobalt ferrite nanoparticles, with a similar trend in SAR with viscosity noted for magnetite nanoparticles although the degree of reduction was less pronounced. This result is reasonable and expected given the conventional understanding of Brownian relaxation. However, a follow up study by Fortin et al. in 2008 further discussed the implications of nanoparticle size and viscosity and how these properties affect Brownian relaxation [20]. The authors note that for nanoparticles with a diameter greater than 5 nm if the viscosity of the carrier medium is larger than approximately 100 mPa.s, a 100-fold increase over water in their words, then the Brownian contribution to heating is effectively null. The body of research into the viscous effects on the specific absorption rate of MNF has yielded a general consensus of the effects with reasonable explanations for deviance from the trend of SAR reduction through Brownian inhibition in a
viscous environment. The size of the nanoparticles contributes substantially to the Brownian relaxation experienced with larger nanoparticles considered as effectively inhibited in highly viscous environments.

1.4 The Effects of Surface Functionalization and pH on Nanoparticle Dispersion

In discussing concentration effects on the heating output of magnetic nanoparticles, the concept of nanoparticle aggregation, or clustering, was presented as a way to account for the disparate heating responses of bare and functionalized nanoparticles. Functionalization meaning the augmentation of the surface of the nanoparticles for some specific purpose dependent upon the application area or desire of the investigator. In general, the notion of capping nanoparticles is to enhance their colloidal stability through alteration of their surface charge typically quantified through zeta potential which provides a measure of the electrical potential at the interface of the nanoparticle and bulk fluid. A 2018 study by Belanova et al. [23] indicates that nanoparticles need to have a zeta potential magnitude greater than 25 mV, either positive or negative, in order to avoid aggregation, however, the exact value producing stability is somewhat in contention. According to information collected by Dheyab et al. in their 2020 paper [24] nanoparticle suspensions with zeta potentials between ± 30 to 40 mV indicate a moderate level of colloidal stability while those between ± 40 to 60 mV have “excellent” stability; with charges below these thresholds indicating a readiness of nanoparticles to aggregate. A study by Bagwe et al. [25] published in 2006 investigated the aggregation and zeta potential of silica nanoparticles with diameters between 80 to 100 nm functionalized with varying concentrations of amine (APTS) and phosphonates (THPMP). Nanoparticles coated with purely APTS demonstrated considerable clustering with DLS measurements indicating effective particle diameters around
2500 nm with a corresponding zeta potential near 0 mV. By adjusting the concentration of ATPS in favor of THPMP the authors demonstrate a reduction in the effective diameter to 115 nm and an enhancement in the zeta potential magnitude to approximately -35 mV. Returning to the 2020 study by Dheyab et al. [24] provides insight into the enhancement of nanofluid stability through the functionalization of 19 nm iron oxide nanoparticles with citric acid. The bare Fe$_3$O$_4$ particles present a Zeta potential value of -31.3 mV with citric acid coated particles denoting an increase in magnitude to -45.3 mV with the authors attributing this enhancement to surface attachment of citrate carboxylate groups. The authors stress the importance of capping iron oxide nanoparticles in order to avoid aggregation which tends to occur due to their large surface energies arising from the high surface to volume ratio with clustering occurring in order to minimize their surface charge, but appropriate functionalization can reduce this tendency by augmenting the zeta potential. Indeed, a 2016 study by Lai et al. [26] presents zeta potential augmentation of iron oxide nanoparticles functionalized with oleic acid (OA) varying from 0 to 1.5 wt% in a liquid medium with a pH of 10. Bare iron oxide particles present a hydrodynamic diameter of 42.96 nm and a corresponding zeta potential of -29.8 mV, but at an OA loading of 0.3 wt% the hydrodynamic diameter increases to 61.04 nm with a zeta potential of – 50.2 mV, demonstrating a marked increase in surface charge. Further increasing the OA loading sees addition charge enhancement with a maximum negative zeta potential of -58.1 mV demonstrated at 1.5 wt% of oleic acid. Interestingly, this study denotes a maximum hydrodynamic diameter at 0.3 wt% of OA with each discrete loading enhancement seeing reductions in effective size with the 1.5 wt% of OA sample presenting a size of 41.9 nm which is remarkably similar to the size of the uncapped nanoparticles. The authors attribute this response to zeta potential enhancement promoting greater stability through electrostatic repulsion brought about by carboxylate ion
attachment to the nanoparticle surface. A 2014 study by Sakulkhu et al. [27] presents the zeta potential of superparamagnetic iron oxide nanoparticles (SPION) in deionized water with varied surface functionalization. The charge of 7.7 nm naked SPIONs was found to be 27.5 mV, with functionalization using variations of polyvinyl alcohol, silicon dioxide, titanium dioxide, and gold all presenting zeta potential augmentation. Gold capped SPIONs with a diameter of 143.9 nm present the greatest magnitude of zeta potential at -48.2 mV. In addition to providing charge values for these variously capped nanoparticles this study presents a measure of the point of zero charge for each nanoparticle treatment which spans from a pH of 3 to 9. In the context of nanoparticles, the point of zero charge is the pH value at which the surface energy of the nanoparticles is equal to 0 mV.

Variations in the surface charge of nanoparticles with differing carrier medium pH has been investigated by multiple studies with results broadly depicting a shift in zeta potential towards a more negative value with increasing pH [28-30]. Variations in how these augmentations are made manifest is dependent upon the chemical interaction of the nanoparticle surface, capping agents, and ions within the carrier medium. A 2016 study by Meng et al. [31] presents the zeta potential of bare iron oxide nanoparticles as a function of pH noting charges of approximately 32.5 and -35 mV at pH values of 2 and 12, respectively. This study also indicates the point of zero charge as falling between a pH of 6 and 7 which corresponds to results presented by Sakulkhu et al. [27] for bare SPIONs. Consideration of pH effects, nanoparticle size, and aggregation is presented in a 2019 study by Godymchuk et al. in 2019 [32]. Two groups of bare Fe₂O₃ nanoparticles with mean diameters of 35 and 120 nm as observed through scanning electron microscopy were denoted as Fe₂O₃-35 and Fe₂O₃-120, respectively. These
particles were dispersed in hydrosol with DLS results presenting a pairing of effective diameter and zeta potential dependent upon the pH of the carrier medium. Zeta potential measurements showed reductions in magnitude for both particle sizes with increasing pH from 3 to 9 with variations in charge observed between the two particle types. At a pH of 3, Fe$_2$O$_3$-35 samples presented a mean zeta potential of approximately 35 mV with Fe$_2$O$_3$-120 samples presenting a charge of roughly 9 mV. However, at a pH of 4 Fe$_2$O$_3$-120 samples see a transition to a negative zeta potential magnitude at a value of roughly -10 mV with Fe$_2$O$_3$-35 samples presenting a zeta potential of roughly 25 mV at this same pH value. Fe$_2$O$_3$-120 samples maintain a negative charge with increasing pH which maximizes around -25 mV at a pH of 7 with comparable charge values presented at pH values of 8 and 9. In contrast, Fe$_2$O$_3$-35 samples reduce in positive charge with increasing pH demonstrating a neutral charge at a pH of 6.5 with negative charge enhancement observed with increasing pH, and a maximum negative zeta potential value of approximately -18 mV obtained at a pH of 9. The presented zeta potential values correspond to observed variations in the effective diameter with Fe$_2$O$_3$-35 and Fe$_2$O$_3$-120 exhibiting diameters of 318 and 344 nm, respectively. Reductions in zeta potential magnitude correspond to increases in the effective diameters which peak for both nanoparticle types at a pH of 6 with Fe$_2$O$_3$-35 seeing mild attenuation in clustering with further pH enhancement, presenting a mean diameter slightly greater than 500 nm at a pH of 9. In contrast, Fe$_2$O$_3$-120 shows a mild reduction in effective diameter at a pH of 7 but demonstrates a considerable decline in clustering with a minimum mean effective diameter of 177 nm observed at a pH of 9. The authors note that Fe$_2$O$_3$-35 nanoparticles demonstrated a greater level of agglomeration than Fe$_2$O$_3$-120 samples in the pH range from 3 to 9 and indicate that smaller diameter nanoparticles tend to more readily cluster than larger particles. Additionally, a 2015 study by Shah et al. [33] presents the effects of pH on
the preparation of iron oxide nanoparticles using the sol-gel method. This study demonstrates the effect of pH on the phase of the iron oxide and the resulting magnetic properties. At a pH of 5 and 7, the nanoparticles produced show a mixed oxide phase of maghemite and magnetite whereas at a pH of 9 only magnetite is found. The authors note decreases in dislocation density and the resulting enhancement of saturation magnetization with increasing pH value.

1.5 The Purpose of this Study

The experiments described and the results presented within this manuscript considers efforts to characterize the thermal output of iron oxide nanoparticles dispersed in varying carrier mediums which have been separated into two categories: magnetic nanofluids and nanoparticle embedded phase change materials (PCM), which undergo a solid to liquid phase change, in an induction heating environment. This demarcation is due to the former subset of effort having been previous published in the journal of Nanoscale and Microscale Thermophysical Engineering and which is presented in its entirety in Chapter 3. This manuscript builds upon this publication through the addition of further induction heating trials using a phase change medium and seeks to analyze and discuss the effects of the carrier medium on the thermal power output with the Brownian contribution to heating being of specific concern. Through investigation of a wide viscosity range of MNF and the onset of a solid-liquid phase change in PCM samples, the Brownian contribution to heating is to be thoroughly characterized. This study will also consider the effects of AMF frequency and nanoparticle concentration in the characterization of the specific absorption rate of nanoparticle samples. The purpose of this study is to build upon the existing body of knowledge and to help further characterize the Brownian contributions during induction heating of iron oxide nanoparticles.
1.6 Chapter Bibliography


CHAPTER 2 Experimental Methodology

Conducting research into the heating output of nanoparticles in an alternating magnetic field requires consideration of the myriad of factors affecting the system. Among these factors the principle considerations for this study are inter-particle interactions, particle and magnetic field interactions, and particle and carrier medium interactions.

2.1 Experimental Variables Considered

The effect on heating output for the first of these factors, interparticle interactions, is made evident through the concentration of nanoparticles within the carrier medium examined. Concentrations of 1, 5, and 10 mg of iron-oxide nanoparticles per 1 ml of liquid or solid-liquid phase change material (PCM) mediums are investigated. Additionally, concentrations of 1, 5, and 10 weight percent (wt%) of nanoparticles per solid-liquid PCM carrier mediums were investigated. The purpose of varying the concentration is to change the mean interparticle distance, which in turn affects how the particles collectively behave. In the theory set up by Rosensweig [1], particle concentration should not have a significant role to play in the heating output of a magnetic iron-oxide nanofluids. However, experiments have shown this to be untrue, with higher concentrations of particles tending to lead to a reduction in the specific absorption rate (SAR) of the system [2-6]. The theory behind this heating degradation with concentration enhancement is the dipole-dipole interaction of particles becoming more pronounced, thereby coupling the magnetic poles of particles, and reducing Néel relaxation. However, this trend with concentration is still a point of contention within the field, where some studies denote heating enhancement with particle concentration [2, 7, 8] which has been discussed previously. The disparate response with concentration may be due to the methods through which the authors of
each study characterize the temperature rise, although this is admittedly speculative at best. An additional concern of interparticle interactions manifests through the clustering of nanoparticles into loose formations and tight chains. While this study does not seek to directly utilize particle clustering as a variable, the degree in which clustering occurs is considered as a measurable value and investigated through dynamic light scattering of low concentration samples.

The particle-field pairing can be examined through varying the peak magnetic field strength and/or the alternating magnetic field (AMF) frequency. Based on Equation 1, both the field strength and frequency play an integral part in determining the heating output of a nanofluid. In the examination of this study, the peak magnetic field strength is fixed at 72.6 kA/m across all samples while the magnetic field frequency is varied between 217, 303, and 397 kHz. Fixing the field strength and varying the frequency was decided due to the capacitors and induction coil on-hand. This setup allowed for an expansive heating output data set relevant across a relatively wide span of field frequencies.

The last factor considered in this study was the nanoparticle interaction with its carrier medium with liquid bases of varying viscosity and solid-liquid PCMs utilized to provide a range of viscosities and solid environments for examination. Aside from Néel relaxation, the other major heat generating mechanism in nanoparticle suspensions is Brownian relaxation. With Brownian relaxation, heat is generated through the physical interaction of individual nanoparticles or particle clusters rotating within the carrier medium. Since the Brownian relaxation constant is directly dependent upon the viscosity of the carrier medium a wide span of viscosities was investigated using blends of deionized water and ethylene glycol as well as
blends of pharmaceutical mineral oil and a commercially available hydraulic fluid blend of naphthenic and paraffinic petroleum. These liquids utilized were chosen due to their viscous properties as to allow SAR trends with viscosity to be captured across a wide span. Water and ethylene glycol were selected to provide a low viscosity range with samples denoted by WEG100, WEG80, WEG60, WEG40, WEG20, and WEG0 with the remaining portion of the solution being ethylene glycol. For example, a WEG100 solution is entirely deionized water while a WEG0 solution is entirely ethylene glycol. Similarly, mixtures of hydraulic fluid and mineral oil were denoted by MH0, MH25, MH50, MH75, and MH100. With MH100 being entirely mineral oil and MH0 being entirely hydraulic fluid. Solid-liquid PCM carriers were investigated to provide an environment where Brownian relaxation would necessarily be inhibited initially but could become a contributing factor post phase change. Paraffin wax and D-Sorbitol also have notably different viscosities in the liquid temperature range of this study which will allow for contrasts in measured heating output. Phase change material samples are simply noted by a letter and their concentration. Examples of this are “P-1mg/ml” which corresponds to a Paraffin base with one milligram of iron oxide nanoparticles per one milliliter of solid PCM, and “S-10wt%” which is a Sorbitol based sample with 10% of the weight accounted for by nanoparticles.

The carrier materials utilized in this study were sourced from multiple suppliers with laboratory grade ethylene glycol purchased from Carolina Biological Supply Company and deionized water supplied in house by an Aries Filterworks Hydra Deionizer. The base oils used were Equate brand pharmaceutical mineral oil sold as a lubricant laxative and NAPA Premium
AW46 Hydraulic Oil. The Paraffin wax purchased came from Aldrich Chemistry, and the 98% D-Sorbitol employed was manufactured by Alfa Aesar.

Figure 1. Images of Procured Carrier Mediums.

2.2 Carrier Medium Characterization

Characterization of the carrier mediums required analysis of the material’s heat capacity, density, and viscosity where applicable. These values were utilized in SAR and theoretical calculations throughout the data analysis. Heat capacity measurements for both liquid and solid-liquid PCMs were taken using the same method of sample preparation and experimental test setup. Sample preparation utilized TA Instruments Tzero hermetically sealed aluminum lids and pans, TA Instruments Die Press, a TA Instruments Differential Scanning Calorimeter (DSC) Model 25, a Sartorius Cubis MSA225S-100-DI digital scale, and a hot plate when applicable. The pans were initially weighed, and the value zeroed on the scale in order to capture the mass of the sample only. For liquid samples, 20 microliter quantities were drawn up and distributed in the pan using a pipette. For solid PCM samples, the Tzero pan was placed on a hot plate set at
100 °C and small quantities of the solid PCM were added a little at a time. Once the material melted and the bottom of the pan was fully covered, the pan was removed from the hot plate and allowed to cool. At this point, the pans were hermetically sealed using the die press. Liquid samples were immediately moved to the DSC for testing while PCM samples were given a minimum of 24 hours to solidify at room temperature. In Trios, the controller software for the DSC, each sample’s mass was input, and a test plan was applied which stepped the temperature down and held an isothermal period of ten minutes at 0°C for oil and PCM samples and 5°C for WEG samples. After the isothermal period, the temperature was raised at a rate of 2°C per minute up to a maximum temperature of 80°C for WEG and oil samples with a maximum of 100°C for PCM samples. These temperature ranges were chosen to avoid any unwanted phase change, such as the freezing or boiling of water, and to entirely capture the appropriate phase change of the PCMs. Additionally, the temperature ramp rate specified was chosen as this was the rate recommended by the manufacturer for calibrating the machine. The data captured was analyzed within Trios for latent heat and melting temperature ranges of the PCM; plots correlating reversing heat capacity and sample temperature data were extracted in an Excel worksheet. Density measurements of each fluid type were taken simply by measuring the mass of one milliliter quantities dispersed from a pipette into a small aluminum pan on an Ohaus Adventurer scale. PCM mass values were obtained from their respective safety datasheets provided by the manufacturer. Viscosity measurements for the liquid samples required the use of multiple instruments in order to accurately measure the viscous properties. A Rheosys Merlin VR rheometer was employed to measure the viscosity of all of the oil samples as well as WEG20 and WEG0 samples. Data collection involved sandwiching a volume of the sample fluid 1 millimeter between the base and a flat disc. The disc was then rotated by the controller software.
and a plot of the viscosity generated. This data was averaged, removing extreme outliers, to determine the sample fluid viscosity. Viscosity measurements of WEG60 and WEG40 samples were collected with a CANNON-Fenske Size 75 Calibrated Opaque viscometer while WEG100 and WEG80 samples were measured with a similar CANNON-Fenske Calibrated Size 25 Opaque viscometer. The two viscometers and rheometer are depicted in Figure 2.

Figure 2. Type 75 Viscometer in Holder on Ring Stand, Type 25 Viscometer and Suction Bulb, and Rheometer.
Operation of the instrument involved suctioning a quantity of the fluid into the holding bulb and corking the larger tube before placing the viscometer in a holder on a ring stand. The instrument was then properly aligned using a level and the cork was removed. The time the fluid took to flow between demarcations on the instrument was recorded and used to calculate the fluid viscosity based on the instruments supplied correlations.

2.3 Nanoparticle Characterization

The nanoparticles utilized in this study were commercially obtained from US Research Nanomaterials and were sold as iron oxide Fe₃O₄ with more than 98% of the particles indicated as having a diameter between 20 and 30 nanometers with a true density of approximately 4.95 g/ml according to the supplier. These particles were chosen due to the relevance of iron oxide nanofluids in a multitude of scientific fields and application spaces. These nanoparticles were subsequently characterized through transition electron microscopy (TEM) and x-ray powder diffraction (XRD). A small quantity of nanoparticles were dispersed into deionized water in a vial and then sonicated in a water bath for 15 minutes. Immediately following sonication, a small volume of the particles was drawn up in a pipette and dispersed on a test slide. This slide was then placed in a container filled with desiccate bags and allowed to dry for 48 hours. TEM imaging was performed on the dry sample using a JEOL JEM-1011 and several images of particles were taken to determine the size distribution. A representative TEM image is provided in Figure 3.
Using the images obtained through TEM, a distribution of particles sizes was manually obtained through ImageJ; a program developed by the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation. ImageJ allowed for direct measurement of the nanoparticle diameters by allowing the user to define the length per pixel of the image. The defined length was set based on the scale bar on the TEM images and manual measurement of
the particles was undertaken. Particle sizes were only measured when a given particle was sufficiently detached from any adjacent particles. This was done to reduce the measurement error due to the lack of clarity in the location of the particle’s edge in tightly clustered particles. The purpose of TEM imaging was to grant an understanding of the actual particle sizes as to compare them with the particle’s hydrodynamic diameter while in suspension. Additionally, theoretical calculations were undertaken using the mean particle diameter determined.

Beyond particle imaging, XRD data was also collected for these particles. However, this measurement was not performed by the author but by a lab collaborator who collected this data using a Rigaku Miniflex II with a 1.541 Å wavelength of Cu Kα radiation. XRD was undertaken to determine the crystalline phase of the particles as to determine their predominant oxide state. Based on the information from the nanoparticle manufacturer it was assumed these particles were mostly Magnetite, as they are specified as \( \text{Fe}_3\text{O}_4 \), but XRD provides the ability to verify if any additional oxide states were present in these particles.

### 2.4 Nanofluid Sample Preparation

Samples using liquids as the nanoparticle carrier medium were prepared by first measuring the appropriate mass of nanoparticles. Weighing paper was first place on a Sartorius Cubis MSA225S-100-DI digital scale and zeroed out. To reiterate, the nanoparticle concentrations analyzed using liquid bases were 1, 5, and 10 mg/ml of carrier fluid. Concentrations of 5 and 10 mg/ml had nanoparticles within ±1% of the noted mass, while 1 mg/ml samples were all verified to be within ±5%. These bounds were chosen to maintain a consistent nanoparticle mass between samples of the same type while allowing for some
variation due to the difficulty in handling dried nanoparticles. After mass measurements were confirmed the particles were transferred to a 1-dram glass vial. Liquid carrier mediums were measured out in 1 ml quantities and dispersed into a vial after the nanoparticles. Blends of the carrier fluid had their constituent fluids measured and dispersed independently of one another with mixing occurring within the sample vial by a gentle swirl. Liquid samples were sonicated in a water bath immediately prior to testing in order to break up particle clusters and better disperse them into suspension. Post sonication, blended fluids were considered adequately mixed as there was no noticeable variation in the fluid. WEG samples received sonication baths at a minimum of 15 minutes, which was deemed sufficient due to the qualitatively adequate dispersion at this exposure time. However, MH samples did not note a sufficient dispersion of nanoparticles at a sonication exposure of 15 minutes and were instead exposed for a minimum of 30 minutes, after which a comparable quality of dispersion was observed. The difference in required sonication time is attributed to the significant viscosity differences of the two liquid types where particle movement is significantly hindered in the oil-based samples. Immediately after sonication, nanofluid samples were moved to the induction heating setup for temperature measurements.
2.5 Nanofluid Characterization

Characterization of the resultant nanofluids was achieved through dynamic light scattering (DLS) on a Brookhaven Instruments ZetaPALS. DLS employs light to measure the diameter of the bodies within a suspension and, in this case, provide a distribution of the measured particle’s effective diameters and the degree of heterogeneity in this distribution in the form of the polydispersity index. However, the opaque nature of the concentrations utilized during induction heating trials did not allow for direct measurement. Samples were instead made
specifically for DLS measurements in concentrations of 0.025, 0.05, 0.1, and 0.25 mg/ml for all WEG sample types, and 0.25 mg/ml for MH100, MH50, and MH0 oil blends. These concentrations were chosen as this range was shown by Lim et al. [9] to most accurately depict particle sizes measured through TEM imaging. The effective particle diameters of the WEG sample types were utilized in a predictive model while oil-based samples provided a point of comparison. DLS characterization was undertaken to provide a measure of the effective particle diameters which will allow for comparisons of particle clustering as a function of viscosity.

2.6 PCM Sample Preparation

Solid-liquid PCM based samples were prepared by first measure a quantity of the PCM on wax weighing paper. These mass was then placed in a 1-dram vial and the nanoparticles weighed based on the quantity for a given sample being made. Paraffin samples have a base mass of 618 mg with created samples falling within ± 1% of this normal value. In order to maintain a similar solid volume, D-Sorbitol samples have a base mass of 1023 mg. These values were chosen as they provide a modest solid volume of approximately 0.7 ml before the introduction of nanoparticles. At a solid Paraffin mass of 618 mg, 1, 5, and 10 wt% samples were measured with normal values of 6.25, 32.5, and 68.65 mg or nanoparticles, respectively, with measured particles masses within ± 3.3% for all concentrations. Similarly, D-Sorbitol samples had nanoparticle masses of 10.33, 53.84, and 113.7 mg, respectively, with measured particle masses within ± 4.3% for all concentrations. Direct comparison of nanoparticles embedded in PCM and nanofluid samples requires comparable loading. To this end, Paraffin and D-Sorbitol samples were made in 0.552 and 0.664 wt% for comparison to 5 mg/ml oil-based nanofluids while the previously discussed 1 wt% PCM samples have a comparable particle loading to 10
mg/ml oil samples. The density reported by the manufacturer in the safety data sheets for Paraffin wax and D-Sorbitol were 900 mg/ml and 1489 mg/ml, respectively. With this information, normal masses of 900 mg of Paraffin and 1489 mg of D-Sorbitol were weighed for sample creation with measured masses within ±0.56% for both PCM types. Once a sample had both PCM and nanoparticles it was transferred to a Corning PC400D hot plate (note: avoid hot plates with magnetic stirrers as these will draw the particles to the bottom of the vial during melting). A depiction of samples heated on the hot plate is given in Figure 5.

Figure 5. Paraffin and D-Sorbitol PCM Samples of Differing Concentration on Hot Plate.
The temperature of the hot plate was raised until the PCM melted and the particles could be dispersed. Dispersion was undertaken with an improvised mechanical stirrer with a 1 mm diameter aluminum rod bent at a right angle at one end and locked in the chuck of a Black and Decker DR260 Corded Drill with a maximum rate of rotation of 1500 RPM. The bent portion of the stir rod is approximately 5 mm in length with the overall length of the rod at 45 mm. The improvised stirrer setup is shown in Figure 6.

![Improvised Stirrer and Samples Cooling in Water Baths.](image)

This dispersion method was chosen due to the difficulty in adequately dispersing nanoparticles through other means. Due to the high melting temperature of D-Sorbitol sonication was impossible with the machine on-hand. Paraffin’s lower melting temperature made sonication possible with an adequately hot water bath, but particle settling was a concern with this method due to the low viscosity of liquid Paraffin. Ultimately, a single method of dispersion was desired,
and the mechanical mixing method was chosen. Once a sample’s PCM was liquefied, that sample was removed from the hot plate and the stir rod inserted into the liquid PCM. The drill was then activated at full speed and moved around in the sample vial for no less than 10 seconds. Samples were considered adequately dispersed once the PCM took on a uniform color and no visible clumps or streaks of nanoparticles could be found on the vial walls. Immediately after dispersion was achieve, the stir rod is removed, and the vial is placed in a beaker of room temperature water. This was done to help quickly reverse the phase change to solidify the PCM and embed the nanoparticles throughout. Quickly placing the dispersed, but still liquid, Paraffin samples in the water bath is very important as the low viscosity can lead to particles settling after only a few minutes. The speed in which D-Sorbitol samples are moved into the water bath is less critical as liquid D-Sorbitol has a much higher viscosity, qualitatively greater than even the oil mediums. Samples were allowed to cool in the water bath for a few minutes until they have visible solidified, and the chance for particles to settle out of the carrier medium is no longer of concern. At this point, 1mm diameter aluminum rods are inserted into center of the D-Sorbitol samples to provide a hole to embed a fiber optic thermocouple; to read the temperature during induction heating. The rod must be embedded while the PCM is still pliant as D-Sorbitol vitrifies during a phase from liquid to solid. Once D-Sorbitol samples completely solidify, the aluminum rod is removed with pliers and the sample is ready to undergo induction heating trials. In contrast, Paraffin samples are much softer in their solid form and a 1 mm aluminum rod is merely inserted into the center of the sample and removed once fully solidified; typically, immediately prior to induction heating. PCM based samples were given 48 hours to fully solidify prior to use in induction heating experiments.
2.7 Induction Heating Setup and Data Collection

Once a liquid sample was appropriately sonicated, and when PCM samples had fully solidified they were moved to the Ambrell EASYHEAT LI 8310 induction heater to measure their thermal response. The induction heater uses a coil with a 35 mm length, an inner diameter of 13.5 mm, and eight turns to heat the samples. As previously mentioned, the maximum field strength is 72.6 kA/m at an alternating current of 401.1 A. By exchanging capacitors within the induction heater magnetic field frequencies of 217, 303, and 397 kHz were achieved using Celem Power Capacitors’ CPRI400New capacitors in 1.0, 0.5, and 0.3 microfarads, respectively. Regardless of the carrier medium, sample vials were nested inside of a small cylindrical 3D printed holder which had a spiral channel built into the external surface through which a polymer tube was wound. The tubing was connected to an air compressor and air was allowed to consistently flow through the line. This was done to thermally isolate the sample as it went to
steady state and during heating, as the induction coil rises in temperature due to the high current cycling required by the process. The coil is cooled internally by chilled water pumped by a Dimplex Thermal Solutions’ Koolant Kooler model number SVI-3000-M which maintains the water temperature beneath 25 °C. Additionally, an external holder was employed which served to vertically position the vial holder in line with the magnetic coil and to help thermally shield the sample from the environment. Figure 8 depicts the heating coil, vial holder, tubing, and external holder with lid.

Figure 8. Induction Heating Coil and Sample Enclosure.
The lid of the external enclosure has a hold through which a small piece of clear tubing was embedded to act as a guide for an Optocon TS3 fiber optic thermocouple. Once a sample was secure in the enclosure, the thermocouple was inserted through the lid and placed within the sample. Fluid samples saw the thermocouple immersed in the liquid in the center of the vial while PCM samples had it inserted into the hole specifically left by the aluminum rod. The embedding procedure of the PCM samples was done in order to accurately reflect the temperature of the bulk of the material instead of merely at the surface. Figure 9 portrays a sample nested within the coil with the thermocouple embedded.

Figure 9. Fiber Optic Thermocouple Embedded in Sample within Coil Enclosure.
Temperature measurements were captured with a Yokogawa UT55A temperature controller and time-temperature plots recorded through the data logging software FoTemp-Assistant2. This setup provided a means by which to visualize the change in the temperature of the specimen, with accuracy up to a tenth of a degree Celsius. The temperature plot of a specimen was observed, and once steady state was achieved, a recorded file of data was initiated, and the induction heater switched on. Figure 10 depicts a screen capture of FoTemp Assistant2 recording data from a sample.
The bottom right plot was used to determine when the sample had achieved steady state temperature while the top right plot is the recorded data for this particular sample. The resulting time-temperature plot was allowed to run uninterrupted until a certain stopping criteria was met. The stopping criteria depended on the purpose of the heating test currently underway with variations between carrier mediums, concentrations, and field frequencies. For example, PCM based samples were exposed to the AMF for as long as was necessary to facilitate the phase change from solid to liquid. In this context, high concentration samples typically achieved this transition more rapidly than low concentrations; with many of the lower concentrations not exceeding the melting point of the material. In general, liquid and PCM samples were exposed to the AMF for no less than 90 seconds. This time was deemed more than adequate as the initial temperature rise is the point of concern for calculations to come, but when a samples was expected to undergo phase change this time was extended as appropriate.

It is worth noting that the heating rate of 5 and 10 wt% D-Sorbitol samples may lead to fracture or breaking of the sample vial during induction heating. This is attributed to the material liquefying more rapidly in the center of the sample, which expands and exerts a force on the still solid portions in the vial. The glasslike nature of the solid material precludes deformation, and this leads to the bottom of the vial gently separating from the wall. Instances of this happening with D-Sorbitol samples were fairly frequent with multiple samples being destroyed in the process. Despite this, the data collected from these cases typically matched samples which survived the process, and as such these failures generally resulted in only the loss of the sample itself. However, if the data from a damaged vial sample was aberrant it was discarded.
2.8 Analyzing Induction Heating Time-Temperature Plots

The plots captured through FoTemp Assistant2 provide a measure of the change in temperature with respect to time for a given sample. This data is exported into a Microsoft Excel worksheet and combined with additional time-temperature plots of the same carrier medium, AMF frequency, and concentration in order to calorimetrically calculate the specific absorption rate of that sample type. Determination of the dT/dt term is less straightforward and requires close analysis of the temperature data. The convention for deciding this value is to apply a linear curve fit to the temperature response; typically, only looking at the data taken within the first 10 seconds after the field is switched on. Plots of the data taken for 10wt% D-Sorbitol at 397 kHz are provided in Figure 11.
The top image in Figure 11 is the temperature data where the first point corresponds to the induction heater turning on. The numbers on the X-Axis are quarter seconds with 40 data points representing 10 seconds of data collection. The slope of the data in the initial few seconds of the plot is the desired portion of the curve, and the bottom image in Figure 11 is the reduction of the
plot to this portion of data with a linear curve fit applied. The displayed slope of these curves is the exact value utilized as $dT/dt$ in SAR calculations. This initial slope is generally distinct from the remainder of the heating curve and is verified visually by the person analyzing the data. Since different samples see differing heating curves, this initial slope may be taken based on the first 1-2 seconds or across the full 10 second period. Typically, samples with a rapid change in temperature are taken across a smaller time step because the initial slope is made manifest sooner. Conversely, samples with a slow temperature rise may not have a distinct initial slope until comparative later in the heating curve. Ultimately, each heating curve will have an initial temperature slope distinct to the combination of concentration, AMF frequency, carrier medium, and AMF field strength applied to that sample which then lends itself to characterization in the form of the calculation of SAR.

2.9 Experimental Results Reporting Explanation

Within the context of this manuscript, reporting the results of experiments on the nanoparticles, nanofluids, and nanoparticle embedded PCMs will be divided into two sections. Results relating to characterization of the nanoparticles and nanofluid samples is presented in Chapter 3 while the PCM based tests are reported in Chapter 4. This is due to Chapter 3 being a standalone, published manuscript reformatted for use in this thesis. Portions of the published manuscript in Chapter 3 reiterate the literature and theory review discussed in Chapter 1 of this thesis.

2.10 Chapter Bibliography


CHAPTER 3 Induction Heating Response of Iron Oxide Nanoparticles in Varyingly Viscous Mediums with Prediction of Brownian Heating Contribution

Co-author: David Huitink, Ph.D.

3.1 Abstract

This study examines the effects of nanoparticle concentration, magnetic field frequency, and carrier fluid viscosity on the induction heating response of nanofluids exposed to an alternating magnetic field. Uncapped iron-oxide nanoparticles with a mean diameter 14.42 nm were sonically dispersed into mixtures of deionized water and ethylene glycol (WEG) as well as highly viscous oil blends. The resulting nanofluids were exposed to an alternating magnetic field with a strength of 72.6 kA/m at frequencies of 217, 303, and 397 kHz with the heating response characterized calorimetrically through the specific absorption rate (SAR). Concentration and frequency effects mirror those found in literature with SAR reduction and enhancement, respectively. Additionally, SAR output is characterized across a wide range of viscosities showing a consistent decrease in heating output as viscosity increases through the WEG regime, however, the SAR was found to be relatively consistent across the oil blends. The effects of particle aggregation were measured through dynamic light scattering denoting particle clustering as a function of viscosity. Viscosity trends with SAR are accounted for by the viscous inhibition of particles reducing their Brownian heating, as well as clustering effects potentially inhibiting heat production in the low viscosity range where aggregation is pronounced. Lastly, a model predicting the Brownian contribution to heating as a function of frequency, concentration, and viscosity is proposed. This study provides a broad view of the effects on heating output for suspensions of commercially available iron oxide nanoparticles for several concentrations and field frequencies across an expansive range of viscosity.
3.2 Introduction

Decades of research in the field of nanomaterials has brought about a wealth of knowledge surrounding the understanding of Magnetic Nanofluids (MNF), and their potential applications. Of principal interest in contemporary research is the utilization of MNFs for the treatment of cancer growth in a process known as Magnetic Hyperthermia. This procedure involves the direct injection of biocompatible MNFs into cancerous cells which are exposed to localized heating brought on by the exposure of the MNF to an Alternating Magnetic Field (AMF). Once the local temperature rises above 42 °C [1] the tumour’s cell wall ruptures and the death of the cancer cells ensues. Therapies of this type have the potential to be less damaging to the body of the patient than contemporary treatments. In order to develop such therapies, a comprehensive understanding of the parameters involved in an MNF, such as the inter-particle interactions of the suspended Magnetic Nanoparticles (MNP), particle interaction with the carrier fluid, particle interactions with the AMF, and clustering effects, must be thoroughly understood. And, to this end, many studies have been conducted to better understand these characteristics.

The principle and commonly understood mechanisms in which MNPs dispersed in suspension induce a temperature rise when exposed to an AMF lie within the viscous interactions of the particles with the carrier fluid - Brownian relaxation and the intra-particle magnetic moment interaction with the AMF - Néel relaxation [2,3]. The time constant calculations of which are given by the following:

\[
\tau_B = \frac{(3\mu V_h)}{(k_B T)}
\]  

(1)
\[
\tau_N = \left[ \frac{\sqrt{K_a V_M}}{2 \sqrt{k_B T}} \right] \tau_0 \exp \left[ \frac{(K_a V_M)}{(k_B T)} \right]
\]

(2)

\[
\frac{1}{\tau} = \left( \frac{1}{\tau_B} \right) + \left( \frac{1}{\tau_N} \right)
\]

(3)

where \( \tau_B \) is the theoretical Brownian relaxation time, \( \tau_N \) is the theoretical Néel relaxation time, \( \mu \) is the carrier fluid viscosity, \( V_H \) is the hydrodynamic nanoparticle volume, \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature, \( \tau_0 \) is a time constant (whose value is typically taken as \( 10^{-9} \) seconds), \( K_a \) is the anisotropy constant, \( V_M \) is the magnetic volume, and \( \tau \) is the effective relaxation time [3-5]. These equations highlight factors influencing the two principle modes of relaxation and more specifically note the distinct parameter affecting Brownian relaxation: carrier fluid viscosity. As viscosity is only one parameter contributing to the overall thermal response of the suspension, the effects of particle concentration, field frequency, and how these parameters elicit variations in the thermal response were also considered.

### 3.2.1 Field Frequency

The effect of magnetic field frequency on specific absorption rate (SAR) has also been researched widely with most data confirming similar trends. At a fixed field strength, Smolkova et al. [6] showed an increase in SAR with field frequency for all concentrations tested. Yoshida et al. [7] also found that SAR enhanced with increasing frequency for their experimental environments; causing a greater heating response at 20 kHz than 3 kHz for field strengths of 3.5 mT and 20 mT. Kim et al. [8] investigated SAR as a function of frequency for field strengths of 150, 200, and 250 Oe and found linear enhancements with frequency for all.
Similarly, Usov and Liubimov [9] showed enhancement in SAR for fields of 100, 200, and 250 Oe with increasing field frequency. SAR enhancement with frequency is clearly shown at the lower two field strengths; however, the 250 Oe field showed a much stronger enhancement with each incremental step in frequency. These studies have shown that frequency influences SAR, but the extent of the effect depends upon other factors, such as field amplitude and the magnetic properties of the samples.

### 3.2.2 Concentration.
Nanoparticle concentration has been a key parameter of interest in developing MNF for hyperthermia, and many studies have been undertaken to determine the trend between concentration and SAR. Conflicting experimental data has shown both enhancements and reductions in SAR for increasing particle concentrations. The experimental results of Urtizberea et al. [10] found SAR enhancement correlated to concentration reduction, and this result was prescribed to inter-particle dipolar interactions inhibiting SAR at higher concentration densities. Additionally, Bakoglidis et al. [11] found a similar trend in SAR in low concentration suspensions, between 0.15 and 1.2 mg/ml, with a suspension of 18 nm iron oxide particles; however, they noted a differing trend for 10 nm particles in the same concentration range. The authors found that SAR increased to a maximum at a concentration of 0.3 mg/ml, but rapidly decreased and remained relatively small for samples at, and above, 0.6 mg/ml. A study by Pineiro-Redondo et al. [1] noted both enhancement and reduction with increasing concentration in their experimental work with uncapped and capped particles. Uncapped magnetite particles had a marked increase in SAR between 0.6 and 10 mg/ml concentrations, while polyacrylic acid capped magnetite particles showed a continuous reduction in SAR for the entire concentration span. The authors ascribe the disparate heating response to colloidal
instability and particle aggregation as the cause for the enhanced heating response seen with the uncapped samples, and attribute dipole-dipole interactions as reducing the thermal output of the capped particles. Deatsch and Evans [12] compiled the experimental work of eleven studies spanning 2005-2012 and expounded upon this lack of consensus. Five of the studies concluded that SAR decreases with concentration, four studies noted an increase, and two concluded that particle concentration has no effect on SAR. Deatsch and Evans conclude that, in the proper context, the studies reviewed suggest that higher particle concentration decreases relaxation time, which would necessarily lead to an increase in SAR; however, the author notes that this not hold true when particles agglomerate at high concentrations.

3.2.3 Viscosity. Viscous effects are the final parameter of interest for this study, and one that has received relatively less focus in research to date. It was noted by Rosensweig [3] that higher heating rates are achieved when Brownian relaxation dominates the system. Referencing Equation 1 makes it evident that the heating response of a system should decrease with increasing carrier fluid viscosity as this increases the time associated with Brownian relaxation, and indeed this effect has been shown experimentally by multiple sources[1, 6, 13]. Pineiro-Redondo et al. [1] developed an equation to estimate the viscosity where heating is maximized based on the magnetic properties of the particles and their hydrodynamic volume. The authors approximated peak SAR for their particles at a viscosity of 22 mPa.s with experimental data maximized near this value. However, it is easy to note that as the hydrodynamic volume increases the viscosity which maximizes heating will steadily decrease. Conversely, as viscosity increases, the Brownian contribution to heating will decrease as well. This leaves Néel relaxation as the sole heating mechanism, thereby resulting in an overall lowered heating response. Zhang
et al. [14] noted a significant enhancement in SAR for magnetite based ferrofluids with increasing fluid viscosity for a limited set of data, but, in general, their work showed a trend toward SAR reduction with increasing viscosity. However, Yoshida et al. [7] state that heating response is strongly linked to viscosity only for low field strength and frequency, and noted that viscosity played a larger role for an AMF field strength of 3.5 mT and a frequency of 3 kHz but had little effect when the frequency was increased to 20 kHz. This same lack of viscous influence was noted for a field strength of 20 mT at both 3 kHz and 20 kHz. Similarly, Usov and Liubimov [9] described two distinct modes of heating where Brownian and Néel mechanisms individually dominate which they called the viscous and magnetic modes, respectively. They described the modes in terms of field strength and stated that viscous forces dominate at lower field strengths.

The purpose of this study is to experimentally measure and discuss the effects of nanoparticle concentration, viscosity, and frequency for a constant field strength on the SAR of powdered iron oxide particles sonically dispersed in suspension. Special emphasis has been placed on experimentally obtaining SAR data across a wide range of viscosities; a focus which has been generally overlooked in most academic studies. Lastly, we wish to present a model to predict the Brownian contribution to the total SAR produced as a function of the previously described parameters.

3.3 Materials and Methods

3.3.1 Carrier Fluid Characterization. Carrier fluids were characterized through their viscosity, density, and heat capacity. Each measurement was taken before the introduction of nanoparticles,
so the values reflect only the carrier fluids themselves. The fluids analyzed were a pharmaceutical grade mineral oil, commercially available hydraulic fluid consisting of a paraffinic and naphthenic petroleum oil blend, laboratory grade ethylene glycol, and deionized water. Trials were performed in pure environments of the fluids as well as specific blends chosen to provide a range of viscosities for comparison. Water-ethylene glycol suspensions are denoted as “WEG” with a trailing number indicating the percentage of water. For example, WEG100 is purely deionized water while WEG0 is entirely ethylene glycol. This naming convention is applied to oil blends as well, where “MH” denotes the percentage of mineral oil within a sample. For viscosity measurements, WEG100 and WEG80 samples were taken using a CANNON-Fenske Size 25 Calibrated Opaque viscometer, WEG60 and WEG40 were measured using a CANNON-Fenske Size 75 Calibrated Opaque viscometer, and WEG20, WEG0, and all oil-based samples were characterized using a Rheosys Merlin VR rheometer. The viscometers utilized only offer measurement accuracy within a specific range of viscosities, thereby necessitating the use of multiple instruments to cover the span of viscosities considered in this study. Fluid density was determined by simply weighing one milliliter quantities on an Ohaus Adventurer AR3130 balance. Lastly, specific heat capacity measurements were taken with a TA Instruments Differential Scanning Calorimeter Model 25. Samples were prepared in hermetically seal aluminum pans, and the reversing heat capacity calculated using a temperature ramp rate of 2 °C per minute.

3.3.2 Dry Particle Characterization. The nanoparticles utilized in this study were purchased from US Research Nanomaterials, and subsequently characterized through x-ray powder diffraction (XRD) and transition electron microscopy (TEM) imaging. XRD results were
obtained using a Rigaku Miniflex II with Cu Kα radiation at a wavelength of 1.541 Å, and microscopy imaging was performed on a JEOL JEM-1011 with samples prepared by sonicating particles in deionized water for 15 minutes, then allowing the nanofluid to evaporate on the test slide.

3.3.3 Sample Preparation. In this study, 99 sample types were prepared by weighing nanoparticles, mixing them into the carrier fluid, and sonicating the samples to disperse the nanoparticles into suspension. Three batches of eleven differently viscous samples were prepared in three particle concentrations for induction heating trials. Sample concentrations were 1mg of nanoparticles per one milliliter of the carrier fluid, 5 mg/ml, and 10 mg/ml. The 1 mg/ml samples were all weighed within +/- 5% in solid weight of nanoparticles per sample while 5 mg/ml and 10 mg/ml samples were within +/- 1%. Dry Nanoparticles were weighed using a Sartorius Cubis MSA225S-100-DI.

3.3.4 Nanoparticle Suspension Characterization. In-suspension particle characterization was performed through dynamic light scattering (DLS) using a Brookhaven Instruments ZetaPALS. Suspension concentrations were analyzed in the range of 0.025 to 0.1 mg/ml as Lim et al. [15] has shown DLS measurements in this concentration range most accurately reflect the particle sizes seen in TEM imaging. All WEG mixtures were examined as well as three oil suspensions: MH0, MH50, and MH100 for comparison. Measurements were taken to determine the effective hydrodynamic diameters of the particles, and these measurements reflect values spanning the range of concentrations specified.
3.3.5 Induction Heating Measurements. Induction heating (IH) of the samples occurred using an Ambrell EASYHEAT LI 8310. The IH setup has an 8-turn coil with an inner diameter of 1.35 cm, and a length of 3.5 cm, and running at 401.1 amperes the coil produces a maximum field strength of 72.6 kA/m. Each of the three sample batches was subjected to a different field frequency during induction heating trials alternating at 217, 303, and 397 kHz. Immediately prior to heating, samples were sonicated to disperse any particles that may have settled while in storage. Samples were then nested within a 3D printed enclosure inside the coil and an Optocon Type TS3 fiber optic thermocouple was inserted into the sample to obtain instantaneous temperature readings through FoTemp-Assistant2. Chilled water was continuously pumped through the coil to remove thermal energy generated during induction heating, and the 3D printed enclosure had tubing wrapped around it to allow airflow to further isolate the sample from the coil.
Figure 1 Induction heating coil and sample.
Once the sample achieved steady state, the temperature measurements began, the magnetic field was switched on, and the temperature response recorded. Data was taken for each sample type multiple times, and the time-temperature response was used to calorimetrically calculate the specific absorption rate as shown in Equation 4.

\[
SAR = \left( \frac{C_p}{\varphi} \right) \left( \frac{dT}{dt} \right)
\]  

(4)

Where \( C_p \) is the specific heat capacity for the carrier fluid, \( \varphi \) the mass fraction of the nanoparticles in suspension, and \( \frac{dT}{dt} \) is the initial temperature change with respect to time [16, 17]. The initial time-temperature response is plotted, and a linear curve fit applied with the slope equating to \( \frac{dT}{dt} \).

3.4 Results and Discussion

3.4.1 Carrier Fluid Characterization. Experimentally measured values of viscosity, density, and heat capacity were taken at 20°C, and the results of the various tests are compiled in Table 1. Comparison of the experimentally determined values to those typically reported demonstrate the accuracy of the measurements. WEG100 samples show error within 2.40%, 0.681%, and 0.478% of reported values for viscosity, density, and heat capacity, respectively, while WEG0 has error values within 6.34%, 0.521%, and 5.33% of those reported. Direct comparison of the oil-based samples is not possible as this data has not been reported.
<table>
<thead>
<tr>
<th>Carrier Fluid</th>
<th>Viscosity (mPa.s)</th>
<th>Density (g/ml)</th>
<th>Heat Capacity (J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEG100</td>
<td>1.024</td>
<td>1.005</td>
<td>4.20</td>
</tr>
<tr>
<td>WEG80</td>
<td>1.816</td>
<td>1.034</td>
<td>3.75</td>
</tr>
<tr>
<td>WEG60</td>
<td>3.11</td>
<td>1.062</td>
<td>3.56</td>
</tr>
<tr>
<td>WEG40</td>
<td>5.33</td>
<td>1.087</td>
<td>2.92</td>
</tr>
<tr>
<td>WEG20</td>
<td>12.48</td>
<td>1.103</td>
<td>2.73</td>
</tr>
<tr>
<td>WEG0</td>
<td>17.12</td>
<td>1.119</td>
<td>2.31</td>
</tr>
<tr>
<td>MH0</td>
<td>171.6</td>
<td>0.869</td>
<td>1.834</td>
</tr>
<tr>
<td>MH25</td>
<td>187.1</td>
<td>0.863</td>
<td>1.828</td>
</tr>
<tr>
<td>MH50</td>
<td>211</td>
<td>0.857</td>
<td>1.865</td>
</tr>
<tr>
<td>MH75</td>
<td>227</td>
<td>0.851</td>
<td>1.886</td>
</tr>
<tr>
<td>MH100</td>
<td>234</td>
<td>0.846</td>
<td>1.934</td>
</tr>
</tbody>
</table>
3.4.2 Particle Characterization.

Figure 2 XRD pattern of nanoparticles utilized.

As evidenced by the inset Miller indices in Figure 2, the measured intensity is commensurate with patterns typically seen for magnetite and maghemite particles in this $2\theta$ range [18, 19]. There is a notable lack of a peak at ~25 degrees indicating the absence of the (2 1 0) crystal plane seen in Maghemite; however, this alone is not enough to rule out the presence of this oxide. And due to the intense similarities in Magnetite and Maghemite XRD patterns it is likely both phases are present. TEM images were imported into ImageJ and analyzed to determine particle size.
distribution. With a sample size of 138, the mean particle diameter was determined to be 14.42 nm with a standard deviation of 4.77 nm. Utmost care was taken when measuring particle diameters, but as one nanometer at this scale equates to two pixels there is a possibility of misrepresenting the particles. As such, it is assumed that individual particle diameters are within +/- 1 nm of the measured value.

Figure 3 Histogram of measured particle diameter with inset TEM image.
Figure 4 provides a plot of the effective hydrodynamic diameters, determined through DLS, showing a prominent trend of decreasing size with increasing viscosity. For samples of WEG100 the average $D_H$ was determined to be 1018 nm, and for WEG0 this was reduced to 349 nm. Further enhancement of viscosity into the oil region shows additional reduction in $D_H$ with average values of 120.1, 122.7, and 116.3 nm for MH0, MH50, and MH100 samples, respectively. The DLS data exhibits effective particle diameters orders of magnitude larger than that of the TEM images with this disparity owed to particles clustering in solution; a commonly associated behavior for uncapped nanoparticles. However, the way DLS techniques measure particle size may be leading to an over emphasis on the largest particle groups. Considering this, it is possible the DLS measurements have over predicted the average particle $D_H$ by not accounting for smaller, less clustered particle groups. Nevertheless, large clusters are presumably the norm at the concentration levels utilized during induction heating trials, but due to the opaque nature of these suspension concentrations direct measurement is not possible through DLS. Additionally, aggregation in the WEG regime could be due to pH-based zeta potential augmentation which has not currently been accounted for in the data presented. While direct pH or zeta potential measurements were not possible for this study, consideration of the pH for the principle carrier fluids will allow us to consider what effects these various mediums have on nanoparticle clustering. As previously discussed studies have presented [20, 21], the point of zero charge, which indicates the greatest readiness for nanoparticles to agglomerate, is considered between a pH of 6 and 7 for bare iron oxide nanoparticles, such as those utilized in this study. In general, deionized water is considered to have a neutral pH of 7, but this value is dependent upon the amount of dissolved carbon dioxide in the fluid and as such the possible range of pH associated with deionized water ranges from 5.5 to 7.5 [22]. Similarly, the pH of
ethylene glycol is considered within a range from 5.5 to 8.0 [23] with Sandengen et al. reporting values between 4.13 and 4.96 at a temperature of 25 °C in their 2007 paper [24]. Mineral oils are considered to have a neutral pH at 7.0 [25], but, unfortunately, the pH of the hydraulic oil utilized has not been reported, thereby stymieing direct consideration of this principle fluid. However, considering the consistent effective diameters observed in the MH0, MH50, and MH100 samples it appears that, if any variation in pH exists between the hydraulic and mineral oils, it is not sufficient to affect the surface charge in a way that would meaningfully augment nanoparticle clustering. Now, considering the WEG regime, the reported pH range could be as wide as 4.13 to 7.5 or as small as 7.5 to 8.0 for WEG100 and WEG0, respectively in both cases. If the pH of WEG100 is close to a neutral value while the pH of WEG0 is more acidic, then the transition from purely deionized water to a purely ethylene glycol environment would mean a transition into a more acidic environment which should enhance the zeta potential of the nanoparticles and reduce aggregation which is probable; however, if WEG100 and WEG0 are of a comparable pH value then other factors may be affecting nanoparticle clustering. Indeed, as previously discussed, the pH of mineral should be approximately neutral, and upon recalling the point of zero charge for iron oxide nanoparticles being between a pH of 6 and 7, it is reasonable to assume that the MH samples should have a pH of a order that denote a low magnitude zeta potential. Given that the presented effective hydrodynamic diameters do not support this hypothesis, there are a couple of possibilities which may better represent the observed trends. Firstly, the varied chemical structures of water, ethylene glycol, and the two oil types may influence clustering in ways not accounted for through pH alone and would require further investigation from a chemistry perspective to characterize these effects. Secondly, the pH of these mixtures could be of a similar degree to where surface charge variations are mild, and the
observed variation in nanoparticle clustering could actually depend more on the viscosity of the carrier medium either allowing or disallowing nanoparticles to migrate in suspension. These possibilities are entirely speculative at current and further investigation is prudent to better understand the effects of the varying chemical environments on the surface charge of bare magnetite/maghemite nanoparticles.

Figure 4 Effective hydrodynamic diameter and Polydispersity Index against carrier fluid viscosity.
### 3.4.3 Induction Heating Response

Figure 5 illustrates the combined effects of frequency, viscosity, and concentration on SAR. The data shows a roughly linear increase in SAR as field frequency increases, but with the limited number of frequencies tested it is difficult to ascribe a linear behavior. Nevertheless, this trend is consistent with the findings previously discussed [8, 9]. Looking at WEG100 samples, the percent increase in SAR from 217 kHz to 303 kHz for 1 mg/ml, 5 mg/ml, and 10 mg/ml concentrations was 23.1%, 60.0%, and 64.5%, respectively. Similarly, the increase from 303 kHz to 397 kHz was 11.0%, 13.5%, and 31.6%, respectively. The data shows a consistent enhancement of SAR with increasing field frequency for the entire viscosity range examined, with modest variations in how this enhancement manifests.

![Figure 5](image-url)

**Figure 5** Experimentally determined specific absorption rate for all samples (grouped by frequency) with inset of oil sample region.
Table 2 Mean SAR Response (W/g) for all samples.

<table>
<thead>
<tr>
<th>Carrier Fluid</th>
<th>µ (mPa.s)</th>
<th>1 mg/ml</th>
<th>5 mg/ml</th>
<th>10 mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>217 kHz</td>
<td>303 kHz</td>
<td>398 kHz</td>
</tr>
<tr>
<td>WEG100</td>
<td>1.024</td>
<td>63.4</td>
<td>78.1</td>
<td>86.7</td>
</tr>
<tr>
<td>WEG80</td>
<td>1.816</td>
<td>57.3</td>
<td>69.0</td>
<td>69.6</td>
</tr>
<tr>
<td>WEG60</td>
<td>3.11</td>
<td>44.6</td>
<td>59.7</td>
<td>61.9</td>
</tr>
<tr>
<td>WEG40</td>
<td>5.33</td>
<td>36.6</td>
<td>43.4</td>
<td>49.3</td>
</tr>
<tr>
<td>WEG20</td>
<td>12.48</td>
<td>27.8</td>
<td>38.6</td>
<td>43.2</td>
</tr>
<tr>
<td>WEG0</td>
<td>17.12</td>
<td>25.2</td>
<td>31.8</td>
<td>37.6</td>
</tr>
<tr>
<td>MH0</td>
<td>171.6</td>
<td>20.1</td>
<td>24.5</td>
<td>35.2</td>
</tr>
<tr>
<td>MH25</td>
<td>187.1</td>
<td>21.1</td>
<td>24.4</td>
<td>33.3</td>
</tr>
<tr>
<td>MH50</td>
<td>211</td>
<td>20.0</td>
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<td>MH75</td>
<td>227</td>
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<td>23.0</td>
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</tr>
<tr>
<td>MH100</td>
<td>234</td>
<td>19.51</td>
<td>21.9</td>
<td>33.1</td>
</tr>
</tbody>
</table>

A consistent trend in the heating response regarding particle concentration is also evident: SAR decreases with increasing concentration for all samples with varying degrees of reduction. A trend well documented in literature [2, 3, 12, 17]. For example, WEG100 samples show a percent decrease in SAR of 11.16% and 36.8% comparing 1 mg/ml to 5 mg/ml and 5 mg/ml to 10 mg/ml samples respectively at 397 kHz, with similar trends seen at 217 kHz and 303 kHz. This result is in line with the explanation of dipole-dipole interactions between particles inhibiting heating as concentration increases, and considering a uniform distribution of particles results in an inter-particle distance 8.52 times the mean diameter, 14.42 nm, for a concentration of 1mg/ml. This distance reduces to 4.98 times the mean for 5 mg/ml with a further reduction to 3.96 times the mean for 10 mg/ml. These values are based on the calculation of the Wigner-Seitz radii assuming a true material density of 4.95 g/cm³ as reported by the manufacturer.
Lastly, the data also shows a marked decrease in SAR with increasing carrier fluid viscosity for all concentrations and frequency pairs examined. As discussed, the cause of this heating reduction is attributed to the inhibited Brownian relaxation experienced by the particles in more viscous environments. Fortin et al. [26] noted that, for particles with diameters greater than 5 nm, above a viscosity of approximately 100 mPa.s, the Brownian contribution is reduced significantly as to be ignored in favor of Néel relaxation. This is not to say there is no Brownian contribution at higher viscosities, but rather that the Néel contribution is far more significant at these viscosities. Indeed, this shift in relaxation dominance manifests itself in the samples above this threshold in this study. The mean standard deviation of the SAR response across all oil samples is merely 0.582 W/g; a notably small value for a relatively wide viscosity range: 171.6 to 234 mPa.s. Comparatively, the mean standard deviation in SAR for all WEG samples is 11.98 W/g on a much smaller viscosity range: 1.024 to 17.12 mPa.s. Calculating the theoretical Brownian response for particles with a mean diameter of 14.42 nm shows the disparate rates of relaxation experienced in the differently viscous mediums.
The theoretical rotational frequencies associated with WEG100 and MH100 samples are 839 kHz and 3.67 kHz, respectively. This denotes a rate of relaxation experienced at the lowest viscosity that is 229 times greater than that experienced by the highest viscosity. Additionally, there is little variation in the theoretical relaxation across the oil samples with the least viscous sample seeing a relaxation rate only 1.37 times greater than the most viscous sample. Since Brownian heating is energy dissipated into the carrier fluid by drag induced during particle rotation, then this reduction in relaxation frequency associated with viscous inhibition explains the relatively consistent heating output seen across oil samples for a particular concentration and
However, we know that, to some extent for uncapped iron oxide nanoparticles (IONPs), particle clustering is linked to the carrier fluid viscosity. With low viscosity samples showing larger particle clusters than those of high viscosity, as evidenced by Figure 4. This finding is not unwarranted as highly viscous carrier fluids inhibit particle movement which should in turn reduce the possibility of large cluster formations post sonication. It is also known that clusters of particles will behave differently than individuals with collective particle interactions affecting the heating output. In fact, several studies have found that particle clustering can result in increased heating output. Dennis et al. [27] showed a seven times enhancement in SAR for dextran capped IONP suspensions with an interaction radius of 70 nm over suspensions with an interaction radius of 200 nm; denoting the ability of clustered nanoparticles working in tandem to enhance heating. Carlton et al. [17] noted a similar increase in SAR with increasing effective diameter for suspensions of TX-100 capped superparamagnetic IONP. Additionally, Serantes et al. [28] analyzed the effects of viscosity on SAR specifically in consideration of dipole-dipole interactions in a water-agar suspension. Their findings showed a decrease in SAR with increasing viscosity for 44nm particles, but, additionally, they found particle chain formations whose lengths were inversely proportional to the concentration of agar. This finding showed that lower viscosity solutions directly resulted in larger cluster formations; a result also seen in this study. Simulations showed particle chain length as contributing to increasing the hysteresis, and therefore enhancing the SAR, which was attributed to preferential magnetic orientations of individual particles through dipolar coupling along the chain. The authors note that optimal heating output will arise when these chains align with the induced magnetic field; a possibility
made difficult in a high viscosity medium. Lastly, based on their simulations, the authors state that SAR growth should lessen with increasing chain length noting that chains of eight particles should be the maximum length where heating output increases. This result showed that there may be an ideal cluster size where SAR enhancement is maximized for a specific MNF system. Indeed, Cabrera et al. [29] found that as 20 nm particles in a 5% agar suspension clustered together, SAR increased up to a maximum of nearly 100 W/g at a $D_H$ of 92 nm. However, further clustering resulted in a significant drop in SAR down to approximately 50 W/g at a $D_H$ of 220 nm. The observed decrease in heating with further clustering may be a result of detrimental dipolar interactions manifesting inside large particle clusters. A parallel effect may be that large cluster formations physically lock particles in place, thereby reducing, or entirely inhibiting, Brownian relaxation for individual particles. The degree to which Brownian, Néel, or even hysteresis mechanism influences the overall heating output is dependent on the degree of clustering experienced by the nanofluid which is, at least in part, dictated by the carrier fluid’s viscosity.

Regarding this study, heating output is plausibly a parallel function of Brownian relaxation of individual particles as well as cluster-based heating mechanisms. Where low viscosity fluids offer less viscous inhibition for free particles resulting in a high output of Brownian based heating while simultaneously providing an environment where clustering is more likely to occur. Given that the effective diameters seen in the WEG samples are much larger than the mean particle diameter measured, it is probable that the large degree of clustering in the low viscosity range is largely inhibiting SAR output as was seen in previous studies [28, 29]. Conversely, the smaller effective diameters of the oil samples might indicate less SAR
reduction, or perhaps SAR enhancement, comparative to WEG samples. Due to the complicated nature of MNFs the exact effects of particle clustering remain unclear, but SAR and DLS data show consistency across the highly viscous oil samples demonstrating that Brownian relaxation is effectively inhibited.

### 3.4.4 Predictive SAR Model

To present a predictive model of the Brownian contribution to heating, Néel based heating must first be isolated and discounted from the overall heating response. Based on the previous discussion, it is reasonable to isolate the Néel based heating for a concentration/frequency pair by averaging the SAR of the corresponding oil samples. Subtracting this value from the SAR of the WEG samples then provides an estimation of the Brownian based heating for that range of viscosities. It is worth reiterating the possibility of particle clustering adversely effecting heating on the low end of the viscosity range, while potentially providing additional heating on the high end. If this is indeed the case, then this model will provide a conservative estimate of the Brownian heating output for an iron oxide MNF system based on the data presented. The proposed model is considered for heating caused by the physical interaction of the nanoparticles with the carrier fluid and the model reflects this by incorporating the Reynolds and Prandtl numbers in the calculation of SAR.

\[
\text{Re} = \frac{(\rho D_h U) / \mu}{\mu} \quad (5)
\]

\[
\text{Pr} = \frac{(\mu C_p) / k}{\mu} \quad (6)
\]
The Reynolds number is the ratio of the inertial and viscous forces in a system, while the Prandtl number is the ratio of the momentum and thermal diffusivity. The $k$ seen in the Prandtl number is the thermal conductivity of the carrier fluid, and the values of thermal conductivity used in this calculation were based on data reported by Bohne et al. [30]. The velocity term, $U$, is the particle velocity as defined in Equation 7 where $\tau_B$ is the theoretical Brownian relaxation stated in Equation 1.

$$U = \frac{\pi D_H}{\tau_B}$$  \hspace{1cm} (7)

These terms are utilized in calculating the SAR for the MNF system in the following way.

$$\text{SAR} = \left(\frac{1}{m}\right) k_B T f_M \text{Re}^\alpha \text{Pr}^{-2}$$  \hspace{1cm} (8)

Where $k_B$ is Boltzmann’s constant, $T$ is the fluid temperature which was considered as 20 °C, $m$ is the mass of an individual spherical particle defined by the $D_H$, $f_M$ is the induced magnetic field frequency in Hz, and $\alpha$ is a term fitted to the experimental data. The alpha parameter was determined by equating the experimental Brownian only contribution to SAR with the parameters listed in Equation 8. Alpha was then curve fit based on sample viscosity and concentration to the fourth order polynomial given in Equation 9.

$$\alpha(\mu, \varphi) = C_0 + C_1 \mu + C_2 \varphi + C_3 \mu^2 + C_4 \mu \varphi + C_5 \varphi^2 + C_6 \mu^3 + C_7 \mu^2 \varphi + C_8 \mu \varphi^2 + C_9 \mu^4 + C_{10} \mu^3 \varphi + C_{11} \mu^2 \varphi^2$$  \hspace{1cm} (9)
The fitted values for $\alpha$ were determined for the discrete range of viscosity and concentration utilized during induction heating trials and these values were utilized in to calculating SAR predictions. Table 3 provides the corresponding coefficients, grouped by frequency, for Equation 9.

Table 3. Fitted parameters for alpha calculation.

<table>
<thead>
<tr>
<th>$f_M$ (kHz)</th>
<th>217</th>
<th>303</th>
<th>397</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀</td>
<td>-1.446</td>
<td>-1.425</td>
<td>-1.394</td>
</tr>
<tr>
<td>C₁</td>
<td>0.1165</td>
<td>0.1074</td>
<td>0.117</td>
</tr>
<tr>
<td>C₂</td>
<td>5.094E-03</td>
<td>-3.270E-03</td>
<td>-1.061E-02</td>
</tr>
<tr>
<td>C₃</td>
<td>-1.661E-02</td>
<td>-1.425E-02</td>
<td>-1.656E-02</td>
</tr>
<tr>
<td>C₄</td>
<td>-1.009E-03</td>
<td>2.395E-04</td>
<td>8.607E-04</td>
</tr>
<tr>
<td>C₅</td>
<td>6.244E-04</td>
<td>1.191E-03</td>
<td>1.356E-03</td>
</tr>
<tr>
<td>C₆</td>
<td>1.147E-03</td>
<td>8.803E-04</td>
<td>1.103E-03</td>
</tr>
<tr>
<td>C₇</td>
<td>6.986E-05</td>
<td>8.429E-05</td>
<td>-1.291E-04</td>
</tr>
<tr>
<td>C₈</td>
<td>-5.767E-05</td>
<td>-2.039E-04</td>
<td>-1.242E-04</td>
</tr>
<tr>
<td>C₉</td>
<td>-2.861E-05</td>
<td>-1.959E-05</td>
<td>-2.599E-05</td>
</tr>
<tr>
<td>C₁₀</td>
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<td>-6.331E-06</td>
<td>1.669E-06</td>
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<tr>
<td>C₁¹</td>
<td>1.844E-07</td>
<td>1.049E-05</td>
<td>9.941E-06</td>
</tr>
</tbody>
</table>

Figure 7 shows a close fit of the predicted SAR to the experimental with a maximum percent error of -9.43% which is seen for the WEG60 sample at 1 mg/ml and 217 kHz.
Figure 7 Percent error associated with predictive Brownian heating model compared to experimental data.

The absolute mean percent error across all samples is 3.28% showing a close approximation to the Brownian only experimental data. It is worth noting, due to the uncertainly inherent in the clustering of particles while in suspension, that this model may result in predictions with error greater than those found in the data presented.

3.5 Conclusions

In this study we have investigated the heating response of uncapped iron oxide nanoparticles with a mean diameter of 14.42 nm sonically dispersed across a broad range of
varyingly viscous carrier fluids. These magnetic nanofluids were prepared in concentrations of 1, 5, and 10 mg/ml and subjugated to induction heating in an alternating magnetic field with a strength of 72.6 kA/m at frequencies of 217, 303, and 397 kHz. The specific absorption rate of each sample was calorimetrically calculated to demonstrate the effects of the key heating parameters of this study. The results showed a quasi-linear SAR enhancement with increasing frequency and a decrease in SAR with increasing concentration. The carrier mediums investigated were water-ethylene glycol mixtures with a viscosity range from 1.024 to 17.12 mPa.s, and oil blends with viscosities spanning 171.6 to 234 mPa.s. Measured SAR outputs exhibited a consistent decrease as viscosity increased through the WEG regime but a nearly consistent heating output was found with the oil samples. The lack of variation in the oil viscosity range demonstrates viscous inhibition of the particles effectively removed any significant Brownian contribution to heating. Dynamic light scattering revealed the degree to which particle clustering occurred and showed the divergence inherent in the two viscosity regimes. Effective diameters decreased through the WEG range but were consistent in the oil range, denoting a diminished degree of clustering at higher viscosities. Since research has shown that excessive particle clustering reduces thermal output, it is concluded that the degree of clustering seen in the WEG viscosity range has inhibited the heating output of those samples. Additionally, it is hypothesized that the mild clustering seen in the highly viscous oil regime may be of an order that enhances the heating output of those samples, or, at the very least, is less inhibitive than the WEG samples. Lastly, a model is proposed that conservatively predicts the Brownian contribution to heating for iron oxide nanoparticles in a viscosity range of 1.024 to 17.12 mPa.s for the frequencies and concentrations examined.
3.6 Acknowledgements

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3.7 Declaration of Interests

The authors have no conflicts of interest to report.

3.8 Chapter Bibliography


3.9 Appendix

Table 4 provides all the values utilized in calculating the theoretical Brownian contribution to heating. The formulae used and the definition of the values was established in the Predictive SAR Model section of the Results and Discussion. This table is provided to allow for ease of access to the data and for further clarification of the values utilized in the predictive model. Viscosity and hydrodynamic diameter are values measured and reported on previously in the paper, whereas the theoretical Brownian relaxation constant, Reynolds number, Prandtl number, and velocity are all calculated values based on Equations 1, 5, 6, and 7, respectively. The mass value, m, is determined by taking the product of the hydrodynamic volume of a sphere, defined by the hydrodynamic diameter, with the mean true density of the nanoparticles reported as 4.95 g/cm$^3$ by the manufacturer. Thermal Conductivity values were estimated by considering data taken from a study by Bohne et al [30] for WEG mixtures with ethylene glycol concentrations of 0%, 25%, 55%, 75%, and 100%. The values associated with these concentrations were first curve fit by temperature to determine values at 20°C. The data associated with solutions of 0% and 100% ethylene glycol were fit to a fourth order polynomial while solutions of 25%, 55%, and 75% were fit to a 2$^\text{nd}$ order power curve. These fits were chosen based on the maximization of R-square values for each fit. The values calculated at 20°C were then curve fit to a 2$^\text{nd}$ order polynomial by concentration to determine the thermal conductivity associated with the WEG concentrations utilized in this study; these discrete values are reported in Table 4.
Table 4. Values utilized in prediction model.

<table>
<thead>
<tr>
<th>Carrier Fluid</th>
<th>Viscosity (mPa.s)</th>
<th>D&lt;sub&gt;H&lt;/sub&gt; (nm)</th>
<th>τ&lt;sub&gt;B&lt;/sub&gt; (s)</th>
<th>U (m/s)</th>
<th>m (g)</th>
<th>k (W/m-K)</th>
<th>Re</th>
<th>Pr</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEG 100</td>
<td>1.024</td>
<td>1017.79</td>
<td>4.19E-01</td>
<td>7.63E-06</td>
<td>2.73E-12</td>
<td>0.600</td>
<td>7.62E-06</td>
<td>7.11</td>
</tr>
<tr>
<td>WEG 80</td>
<td>1.816</td>
<td>848.73</td>
<td>4.31E-01</td>
<td>6.19E-06</td>
<td>1.58E-12</td>
<td>0.494</td>
<td>2.99E-06</td>
<td>12.76</td>
</tr>
<tr>
<td>WEG 60</td>
<td>3.11</td>
<td>564.42</td>
<td>2.17E-01</td>
<td>8.17E-06</td>
<td>4.66E-13</td>
<td>0.406</td>
<td>1.57E-06</td>
<td>23.92</td>
</tr>
<tr>
<td>WEG 40</td>
<td>5.33</td>
<td>510.24</td>
<td>2.75E-01</td>
<td>5.83E-06</td>
<td>3.44E-13</td>
<td>0.336</td>
<td>6.07E-07</td>
<td>39.71</td>
</tr>
<tr>
<td>WEG 20</td>
<td>12.48</td>
<td>323.75</td>
<td>1.64E-01</td>
<td>6.19E-06</td>
<td>8.80E-14</td>
<td>0.283</td>
<td>1.77E-07</td>
<td>106.16</td>
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<tr>
<td>WEG 0</td>
<td>17.12</td>
<td>348.86</td>
<td>2.82E-01</td>
<td>3.88E-06</td>
<td>1.10E-13</td>
<td>0.247</td>
<td>8.86E-08</td>
<td>158.20</td>
</tr>
</tbody>
</table>
CHAPTER 4 The Thermal Response of Nanoparticle Embedded PCMs in Solid and Solid-Liquid Phase Change Environments

Nanoparticle induction heating of MNF has been a widely explored topic over the past decades with a significant body of research. The investigation of nanoparticles embedded in PCMs has also been a subject of study over the past decade. However, this body of research has been generally concerned with the enhancement of thermal properties of the PCM in order to better leverage the thermal energy storage potential of a solid to liquid phase change in the form of latent heat [1-4]. This portion of the study investigates the induction heating response of the same batch of nanoparticles characterized previously embedded in Paraffin wax and D-Sorbitol PCMs. This effort will allow for a better characterization of the Néel relaxation contribution to heating through the assumption of true Brownian inhibition for the PCM in a solid state.

4.1 PCM Carrier Medium Characterization

<table>
<thead>
<tr>
<th>PCM Base</th>
<th>Specific Heat Capacity (J/g°C)</th>
<th>Main Phase Melting Temperature (°C)</th>
<th>Enthalpy of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin Wax</td>
<td>2.44</td>
<td>55.7</td>
<td>180.4</td>
</tr>
<tr>
<td>D-Sorbitol</td>
<td>1.909</td>
<td>75.7</td>
<td>94.9</td>
</tr>
</tbody>
</table>

Table 1 provides the averaged results from the Differential Scanning Calorimetry tests on pure PCM carrier mediums. The measured values for Paraffin Wax are well aligned with those reported in literature with typical heat capacity values ranging from 2.0 to 2.981 J/g°C, latent heat values range from 86 to 266 J/g, and melting temperatures were observed from 30 to 75 °C depending on the source [5-9]. Heat capacity measurements of D-Sorbitol track with those reported in literature which tend to range from 1.325 to 2.5 J/g°C [9-13]. Typical melting
temperature values for D-Sorbitol tend to range from ~80 to 99.2 °C with latent heat of fusion values in the range of ~121 to 185 J/g [9, 10, 12, 13]. The melting temperature and enthalpy of fusion values observed in this study most closely resemble results discussed by Liu et al. [13] which noted two endothermic peaks during DSC analysis of pure D-Sorbitol samples resulting in a combined latent heat of approximately 121 J/g; a value 27.5% greater than the enthalpy of fusion reported in this study.

As evidenced by Figure 12, both Paraffin and D-Sorbitol samples investigated in this study contained two endothermic peaks denoting different phases of the PCM melting at different temperatures. While the main phase of the PCM constitutes the vast majority of the sample the
minor phase still contributes to the thermal response, and, as such, the enthalpy of fusion reported includes both phases. Paraffin samples have minor peaks at approximately 36.7 °C and major peaks at 55.6 and 55.8 °C for trials 1 and 2, respectively, with the latter values averaged as the main phase melting temperature. These minor and main phase peaks are well within the melting temperature bounds stated in the literature previously discussed [5-9]. Likewise, D-Sorbitol sees two sets of endothermic peaks with trial 1 having a minor peak at 48.2 °C and a major peak at 75.7 °C while trial 2 of D-Sorbitol demonstrates a lessened minor peak at 45.7 °C with a major melting peak at 75.7 °C. As previously stated, the D-Sorbitol results of this study most reasonably correspond to results published by Liu et al., although minor and major melting temperatures occur around 55 and 80 °C in the cited study [13].

4.2 Spatial Heating Evaluation of Nanoparticle Embedded PCMs

Given that temperature readings acquired during induction heating occur with the use of a single fiber optic thermocouple embedded in the center of a sample, it is important to establish if these readings are reasonably representative of the overall temperature of the sample mass. To this end, video was taken of samples during induction heating to provide a visual description of the melt propagation with respect to the measured temperature. Figure 13 provides images of a 1 wt% sample of D-Sorbitol exposed to a 303kHz field frequency.
The pictures of the melt progression provided in Figure 13 have had their brightness and contrast adjusted to help expose variations in the PCM regarding the phase change. As evidenced by Figure 13, changes in the sample surface become noticeable at the 360 second mark where a temperature of approximately 73 °C is recorded. A gradual melt at each time step thereafter is observed with a fully liquid sample achieved around the 720 second mark which corresponds to a temperature reading of 87 °C. The temperatures recorded at the onset and cessation of the solid-liquid transition of the PCM are consistent with the heat flow curves of D-Sorbitol in Figure 12 and denote the measured temperature as being representative of the entire sample at 1 wt%.
Similarly, in Figure 14, D-Sorbitol at 10 wt% and 303kHz denotes the onset and cessation of surface melting at 20 and approximately 35 seconds corresponding to temperature readings of approximately 60 and 84 °C, respectively. The onset of the phase change occurs at a lower temperature of the bulk measurement than the 1 wt% sample but occurs sooner and sees a more rapid melt; with the entire phase change occurring in less than 20 seconds. Localized temperature variations within the PCM are likely due to the varying degree of particle dispersion for a particular sample. However, the bulk temperature recorded by the fiber optic thermocouple once again indicates a reasonable characterization of the 10 wt% sample as a whole based on the comparison of the sample’s time-stepped imaging response. Examination of the extremes regarding particle loading, and their closeness in transient temperature profiles leads to the reasonable characterization of D-Sorbitol samples through the embedded fiber optic thermocouple.
In consideration of the melt progression of Paraffin based samples, it is important to recall that nanoparticles are mechanically dispersed while the PCM is in a liquid state. As the Paraffin is rapidly chilled it solidifies faster at the edges with the center portion the last part to undergo the transformation. Because of this method of sample preparation, the PCM takes on a somewhat bowl like shape in the sample vial.

Figure 15. Paraffin 10 wt% Sample Removed from Vial.

Figure 15 depicts a solid Paraffin sample which has been removed from its vial to better showcase the shape of this PCM type post sample preparation. The diameter of the sample is approximately 13.25 mm, and the central meniscus of the solid sample is typically less than 4
mm below the outer most portion where it contacts the vial wall, and despite the shape of the sample the majority of the PCM exists below this section.

Paraffin 1 wt% in a 303kHz frequency AMF, depicted in Figure 16, begins to show some signs of melt in the central portion of the sample where the thermocouple is embedded around the 60 second mark, and as the temperature rises the sample begins to show signs of isolated melting at the surface with a significant portion of the sample in the process of changing phase around the 270 second mark. The sample continues to melt first as the bulk, bottom portion, of the sample changes phase and particles are drawn out of suspension into clusters which migrate towards the edges of the vial, and the portion of the sample which clings higher to the walls is generally the last portion to melt. The onset of the Paraffin phase change begins around 40 °C which corresponds to the minor, subphase, melting peak in Figure 12 with the 270 second mark occurring at a bulk temperature of 57 °C, slightly above the peak melting temperature of the main phase Paraffin base. Interestingly, a mild shift in color is noted in the Paraffin sample as it
is heated over time. This is attributed to nanoparticles being drawn out of suspension and into clusters which migrate towards the edge of the vial to better align with the magnetic field.

Due to the lower viscosity of liquid Paraffin the nanoparticles can easily leave suspension and form into long cluster chains as depicted in Figure 17. Prior to heating the 1 wt% Paraffin sample on the microscope slide was consistently dark brown throughout. However, as the sample began to melt the nanoparticles were pulled out suspension leaving the semi-transparent white color of the base Paraffin, and the portions of the slide where the sample is still brown in color is where the PCM did not undergo a phase transition. In the central portion of the sample the nanoparticle chains align with the magnetic field to form multiple particle lines, however, quantities of particles were drawn towards the edges of the slide where they aggregated into larger masses.
corresponding roughly with the spacing of the induction coil. On the bottom of the slide it is visible where the nanoparticles once clustered, but these particular particles were drawn off of the slide and stuck to the coil. The behavior exhibited by the particles on the slide sample help to explain why the sample in Figure 16 seems to grow lighter in color over time. As the sample melts the nanoparticles are largely drawn out of suspension into tight clusters which migrate towards the edge of the vial and form long chains.

This shift in nanoparticle dispersion draws the bulk temperature reading into question, therefore imaging of these samples was undertaken using a FLIR thermal camera to validate the thermocouple reading. Figure 18 depicts transient temperature rise of a sample of 1 wt% Paraffin across a seven-minute time span taken through top down thermal imaging.

![Figure 18. Boxplots of the Transient Temperature Distribution of Paraffin 1 wt% in a 303kHz AMF. The inset image depicts the layout of the points of temperature measurement.](image)
The blue diamonds and associated dash line mark the mean temperature at each time step, and the five temperature points of measurement were taken at the sample center, Sp1, and at cardinal locations towards the edge of the vial with Sp2 through Sp5 corresponding to North, East, South, and West, respectively. Table 2 contains the temperature values depicted in the boxplot in Figure 18 with mean and standard deviation values calculated.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
<th>300</th>
<th>360</th>
<th>420</th>
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<tbody>
<tr>
<td>Sp1</td>
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<td>54.7</td>
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<td>52.9</td>
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<td>51.5</td>
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<td>2.91</td>
<td>1.92</td>
<td>2.08</td>
<td>2.64</td>
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</tbody>
</table>

The maximum standard deviation given in Table 2 is 2.91 °C and occurs at 120 seconds. The standard deviation fluctuates slightly between each time step and demonstrates a value of 0.853 °C at 420 seconds when the sample is fully liquid. The variation in the temperature distribution is attributed to the bowl-like shape of the Paraffin which is supported by the slightly higher temperature associated with reading Sp1. Overall, the central temperature reading portrayed in Table 2 tracks closely with the readings from the embedded thermocouple in Figure 16, and the mild variation in temperature associated with the shape of the sample lends credence to using the thermocouple data to characterize the SAR of 1 wt% Paraffin samples.
Figure 19 presents a 10 wt% sample as it melts over time with the corresponding embedded thermocouple temperature plot. A visible melt begins prior to the 5 second mark which corresponds to a temperature of approximately 37 °C. This initial melt is similar to the 1 wt% sample which noted the initiation of the solid-liquid phase change at a temperature consistent with the minor Paraffin subphase shown in Figure 12. The majority of the sample indicates a total transition into a liquid state at 30 seconds, at a measured temperature of 118 °C, with any remaining PCM stuck to the wall entirely melted at 35 seconds. It is appropriate to note that the low liquid Paraffin viscosity led to the thermocouple drifting and coming into contact with the glass of the vial around the 20 seconds into the heating. This was manually rectified with tweezers and the thermocouple moved back to center at the 23 second mark as indicated by the abrupt temperature change. The temperature curve in Figure 19 is reflective of the difficulty in
properly imaging the melt of 10 wt% Paraffin samples with an embedded thermocouple. Even while manually holding the thermocouple from the beginning of an induction heating trial it proved difficult to obtain a consistent temperature curve. Despite this, the onset of melting, and the rapid transition into a liquid state is consistent with the data previously observed. Additionally, it is important to note that error induced through thermocouple drift is a complication only present with samples heated for the express purpose of visualizing the melt. During typical data collection the lid of the induction coil enclosure acts as a guide for the thermocouple and keeps it well centered. Figure 20 depicts the temperature distribution in a 10 wt% sample taken through a thermal camera with a top down view.

Figure 20. Boxplot of the Transient Temperature Distribution of Paraffin 10 wt% in a 303kHz AMF. The inset image depicts the layout of the points of temperature measurement.
Figure 20 uses the same temperature reading layout as previously described for Figure 18, and the mean and standard deviation of the data presented is tabulated in Table 3.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp1</td>
<td>25.7</td>
<td>51.0</td>
<td>57.6</td>
<td>87.3</td>
<td>97.3</td>
<td>105.9</td>
<td>113.2</td>
</tr>
<tr>
<td>Sp2</td>
<td>25.8</td>
<td>49.3</td>
<td>55.1</td>
<td>81.3</td>
<td>99.3</td>
<td>107.3</td>
<td>116.1</td>
</tr>
<tr>
<td>Sp3</td>
<td>25.7</td>
<td>46.6</td>
<td>53.5</td>
<td>76.4</td>
<td>94.0</td>
<td>106.0</td>
<td>117.8</td>
</tr>
<tr>
<td>Sp4</td>
<td>25.8</td>
<td>48.3</td>
<td>54.4</td>
<td>79.5</td>
<td>93.0</td>
<td>102.9</td>
<td>111.0</td>
</tr>
<tr>
<td>Sp5</td>
<td>25.7</td>
<td>49.1</td>
<td>55.0</td>
<td>80.5</td>
<td>96.3</td>
<td>106.0</td>
<td>115.7</td>
</tr>
<tr>
<td>Mean</td>
<td>25.7</td>
<td>48.9</td>
<td>55.1</td>
<td>81.0</td>
<td>96.0</td>
<td>105.6</td>
<td>114.8</td>
</tr>
<tr>
<td>Std. Dev</td>
<td>0.0548</td>
<td>1.601</td>
<td>1.525</td>
<td>3.98</td>
<td>2.53</td>
<td>1.627</td>
<td>2.67</td>
</tr>
</tbody>
</table>

The maximum standard deviation in the data presented in Table 3 occurs at the 30 second mark with a value of 3.98 °C which is comparable to the spread of the 1 wt% Paraffin samples but occurs over a much shorter time span. Indeed, despite any error introduced during video imaging through thermocouple drift the temperature distribution of 10 wt% samples indicates a relatively consistent temperature throughout the sample especially during the initial solid phase heating and when the sample became fully liquid above the 40 second mark. Still, it is worth noting the variations in temperature readings between Figure 19 and Figure 20. Both samples began at temperatures below 30 °C and were heated to a comparable level by the 10 second mark but depart in temperature readings from this point. This variation could be due to a combination of the location of measurement and the drift/manual handling of the thermocouple.
4.3 Solid State PCM Induction Heating Results

Figure 21. Experimentally Determined Specific Absorption Rate for 1, 5, and 10 wt% Samples.

<table>
<thead>
<tr>
<th>Carrier PCM</th>
<th>1 wt%</th>
<th>5 wt%</th>
<th>10 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin Wax</td>
<td>12.47</td>
<td>3.13</td>
<td>2.40</td>
</tr>
<tr>
<td>D-Sorbitol</td>
<td>10.90</td>
<td>2.94</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Table 4. Mean SAR Response of Solid State PCM

<table>
<thead>
<tr>
<th>Carrier PCM</th>
<th>1 wt% kHz</th>
<th>5 wt% kHz</th>
<th>10 wt% kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin Wax</td>
<td>217 kHz</td>
<td>303 kHz</td>
<td>397 kHz</td>
</tr>
<tr>
<td>D-Sorbitol</td>
<td>12.47 kHz</td>
<td>14.16 kHz</td>
<td>15.76 kHz</td>
</tr>
</tbody>
</table>

Figure 21 provides a plot of the mean SAR results with error bars while Table 4 provides the mean values of the plotted data for Paraffin and D-Sorbitol samples in 1, 5, and 10 wt%. The values of the X-axis in Figure 21 are based on the mean value of that sample type as measured during the creation of those samples. As evidenced by Figure 21 and Table 4, the calculated SAR values are close in magnitude when comparing PCM carrier mediums, with minor variations.
made manifest. The trends in SAR for solid PCM carrier mediums mimic those of the nanofluids; increasing concentration led to decreases in SAR and increasing the frequency denotes mild SAR enhancement. At 5 and 10 wt the SAR output is markedly lower than that delivered in the nanofluid samples, owing to the extremely pronounced interparticle dipole-dipole interactions. This is made clear in the comparison of 1 and 10 wt% samples for a particular frequency with Paraffin based samples at 217 kHz showing a roughly 5.2 times SAR output at 1 wt% over 10 wt% samples, and D-Sorbitol samples saw a 5.67 times SAR output for the same sample types and frequency.

Notably, Paraffin Wax and D-Sorbitol samples output similar SAR across concentrations and field frequencies. This denotes the high probability of physically inhibited particles leading to the cessation of Brownian relaxation, and, in this case, Néel relaxation would exist as the exclusive heating mechanism for the PCM embedded nanoparticles. The comparable SAR of Paraffin and D-Sorbitol samples is owed to the exclusivity of Néel based heating which is generally unaffected by the carrier medium. However, this is not entirely accurate as the properties of the carrier medium have a direct effect on the quality of dispersion achieved during sample preparation. Indeed, the mild variation in SAR between Paraffin and D-Sorbitol samples is likely owed to the differing quality of dispersion achieved with each sample base. In a liquid state, D-Sorbitol has a syrup-like consistency and viscosity which lends the medium a superior ability to maintain particles in suspension, due to their viscous inhibition, but this benefit comes at the cost of greater difficulty in dispersing the particles. In contrast, liquid Paraffin has a much lower viscosity, offering ease of particle dispersion, but also rapid precipitation. These differences in the liquid states of the carrier mediums during sample preparation lead to variance
in particle dispersion which should account for the mild differences in SAR output in the solid PCM state. However, as the samples rise in temperature and the solid to liquid phase change occurs, the shift towards a combined Néel and Brownian system should manifest itself in the heating curve. In this combined regime, Brownian relaxation would contribute to the heating output according to the properties of the liquid state of the carrier medium. As previously stated, the high viscosity of liquid D-Sorbitol should disallow any major contribution through Brownian relaxation, while liquid Paraffin should demonstrate an increase in heating output.

4.4 PCM Phase Change and SAR Response

The top plot of Figure 22 depicts two representative temperature curves of 5 wt% Paraffin based samples at 217 kHz, and the bottom plot depicts D-Sorbitol samples at the same frequency.
concentration and frequency. This concentration and field frequency pair was chosen to discuss variations in the heating output post phase change because they produced temperature curves with distinct phase regions which easily lent themselves to analysis. The “Initial Slope” called out in the plots is the dT/dt value utilized to calculated solid state SAR, as expressed in Table 4. Note that the curves depicted in Figure B are only a portion of the samples used in the calculation of SAR but serve as representative curves for their sample type as they feature distinct phase regimes. The initial slope value is meant to depict the sample’s heating output in the first moments of exposure to the induction heater and is comparable to the values utilized in the calculation of SAR for the nanofluid samples in time-span and justification.

<table>
<thead>
<tr>
<th>PCM Base</th>
<th>Liquid Specific Heat Capacity (J/g°C)</th>
<th>Standard Deviation (J/g°C)</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>2.39</td>
<td>1.682E-02</td>
<td>65-70</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>2.72</td>
<td>6.04E-03</td>
<td>85-90</td>
</tr>
</tbody>
</table>

As evidenced by the data in Table 5, the liquid phase of D-Sorbitol has a markedly higher heat capacity compared to its solid phase; a 42.5 percent increase for values averaged from 85 to 90°C. Comparatively, Paraffin demonstrates a mere 2.05 percent decrease in specific heat capacity across a temperature range from 65 to 70 °C. Heat capacity averages were taken to provide a reasonable value for calculating the liquid phase SAR using data across a relatively wide temperature range to accommodate a reasonable fit of the linear slope. It is important to notice that the liquid slope regions begin within the melting temperature range recorded during heat capacity trials. As a consequence, dT/dt values of the specified “Liquid Phase Slopes” were considered between 64.9 and 70.3 °C for both Paraffin samples, and 85.0 to 90.3 °C and 84.8 to 90.2 °C for D-Sorbitol samples 1 and 2, respectively. These bounds were chosen because they
are outside of the melting temperature range observed in Figure 12 where the liquid phase heat capacity values were consistent and could be reasonably averaged for calculation. The mean liquid slope for 5 wt% Paraffin samples within this range is 0.2437 and the resulting liquid state SAR is calculated as 11.44 W/g, and the mean slope for 5 wt% D-Sorbitol samples is 0.2072 with a resulting liquid state SAR of 11.37 W/g. Both samples indicate a more than 3.5 times increase in heating over their values reported in Table 4 which utilizes their “Initial Slope” in the calculation of SAR. However, extending the curve through the solid phase region up to the point where the minor phase of the PCM begins to melt provides results that are decidedly different than considering only the initial slope.

For Paraffin wax, the minor phase has an onset of melting temperature around 25 °C, and by extending the linear curve fit up to 24.7 and 25.4 °C for samples 1 and 2, respectively, we see the “Extended Solid Phase Slope” values called out in Figure 22 which average to be 0.2066 °C/s with a corresponding SAR value of 9.90 W/g. Similarly, D-Sorbitol begins to see the onset of melting in its minor phase around 32 °C, and extending the curve fit out to 31.6 and 31.7 °C for samples 1 and 2, respectively, sees an average dT/dt of 0.3286 °C/s and an SAR value of 12.64 W/g. These values are also markedly higher than those reported in Table 4 for these sample types, and more closely resemble the liquid phase SAR values calculated. The onset of Brownian relaxation in the Paraffin 5 wt% sample sees an increase in the SAR of 1.54 W/g which is a percent increase of 15.6 % over the assumed Néel only relaxation in a solid phase. This result was expected as the liquid viscosity of Paraffin at 70 °C is reported to be between 5.48 and 6.7 mPa.s [14, 15], a value comparable to WEG40 at 20 °C. An additional source report the kinematic viscosity of Paraffin wax at 100 °C which, for a density of 900 kg/m³, equates to
approximately 3.69 to 4.86 mPa.s which is in alignment with the previous sources when adjusting for temperature [16]. In contrast, D-Sorbitol was not expected to increase in heating output in a liquid state due to its extremely viscous nature. The viscosity of liquid D-Sorbitol was investigated by Angell et al. [17] and can be calculated by the following equation for a temperature range between -23 and 100 °C.

$$\mu = 0.019 \exp\left[\frac{1832}{(T - 212)}\right]$$  \hspace{1cm} (7)

In this equation $\mu$ is the dynamic viscosity in mPa.s and T is the temperature of the liquid D-Sorbitol in units of Kelvin. Using Equation 7, the calculated viscosity of D-Sorbitol at 90 °C equates to a value of 3488 mPa.s, approximately 523 to 636 times more viscous than liquid Paraffin at 70 °C. Indeed, the 5 wt% D-Sorbitol samples saw a drop in SAR of 1.27 W/g, a 10 % decrease in heating output. Based on the apparent viscosity of liquid D-Sorbitol it is a reasonable assumption that no Brownian relaxation occurs post phase change and as such there is no increase as seen in the Paraffin samples. However, the noted decrease could be attributed to an observation exclusive to D-Sorbitol where the sample presents a sort of constriction in the presence of the AMF.
Figure 23. D-Sorbitol at 10 wt% Constricting in the Presence of a Magnetic Field.

Figure 23 presents a 10 wt% sample of D-Sorbitol already in a liquid state that is exposed to the AMF at 303 kHz with the observed change occurring over 1 to 2 seconds with the observed shape maintained until the AMF was shutdown. The image contrast of Figure 23 has been adjusted in order to better visualize the response. A 10 wt% sample was chosen for imaging due to it showing a greater level of constriction than lower concentrations, and the difficulty associated with visualizing the movement precluded capturing modest movements at lower concentrations. Despite best attempts, still images of the constriction fail to adequately capture the movement of the sample, but the motion observed is one where the sample is drawn down and out to the edges of the vial, and this is reminiscent of the way nanoparticles cluster and migrate to the edges of the vial in the liquid Paraffin samples to better align with the magnetic field. However, due to the extremely viscous nature of liquid D-Sorbitol, particle precipitation is unlikely, but the presented motion seems to indicate a level of alignment with the AMF which augments the shape of the carrier medium without settling of the nanoparticles. This effect could
explain the drop in SAR observed for liquid D-Sorbitol if the constriction produces an effect similar to a localized increase in concentration, although further examination would be required to justify such a claim. Potential drawbacks of extending the solid phase curve could be the blind introduction of localized Brownian relaxation as you approach the minor phase melting temperature, and, depending on where you make the cutoff on the curve fit, the dT/dt value can be significantly varied outside of the “Initial Slope” portion of the curve. However, while this may prove detrimental to the analysis of nanofluids, where particle settling can occur over time, extending the curve fit of dT/dt up to a point prior to the onset of a phase change may be a better representation of the heating output of the solid PCM sample. A justification for this postulation is the similarity between the liquid and extended solid phase SAR outputs of D-Sorbitol. Without extending the D-Sorbitol curve fit of the slope, the marked increase in SAR in a liquid phase does not intuitively make sense. Although, when considering direct comparison of PCM samples and nanofluids, the “Initial Slope” convention must be maintained for consistency.

Regardless of which solid phase slope is applied, D-Sorbitol and Paraffin samples in a liquid state demonstrate a comparable level of heating output despite the onset of Brownian relaxation in the latter sample type. This may be owed to the pronounced settling, clustering that occurs in a low viscosity environment with these types of powdered nanoparticles.
Figure 24. Left: 5 wt% Paraffin and D-Sorbitol Samples Immediately Prior to Induction Heating. Right: 5 wt% Paraffin and D-Sorbitol Samples Post Induction Heating.

The left image in Figure 24 shows 5 wt% samples of Paraffin and D-Sorbitol as they are immediately prior to being placed in the sample holder of the induction heater while the right image depicts these same samples post induction heating. As is evident in the image, pronounced nanoparticle settling occurs in the Paraffin sample during its liquid phase with a noticeable color shift while the D-Sorbitol sample indicates a similar level of particle dispersion before and after heating. Both samples were heated well above their melting temperatures with Paraffin and D-Sorbitol samples reaching maximum temperatures of 109.9 and 140.3 °C, respectively. As was discussed in the results section of Chapter 3, nanoparticle clustering may well be impeding the heat output of Paraffin samples due to the decreased interparticle distance resulting in greater dipole-dipole interference. Additionally, the close proximity of settled particles could be inhibiting Brownian relaxation but the degree to which this occurs is unclear. The 1.54 W/g increase in the SAR of the Paraffin samples attributed to the onset of Brownian relaxation could be only a portion of the actual Brownian contribution to heating. The theoretical Brownian
relaxation experienced for an idealized spherical particle with a diameter of 14.42 nm equates to 6.64E-06 seconds for liquid Paraffin at 70 °C, taking the viscosity as 6.68 mPa.s. At this size of particle and carrier viscosity Brownian relaxation should contribute a significant portion of the overall heating output, however, this is not evident in the modest increase observed. Due to the similarity in heating output, the combined effective relaxation constants of the liquid state samples should be roughly equivalent given the similar heat capacities and nanoparticle concentrations. Realistically, variations in the quality of nanoparticle dispersion within the samples post melt make direct comparisons somewhat tenuous, but reasonable assumptions should provide for a basis of comparison. If nanoparticle settling in the D-Sorbitol samples can be largely ignored, then it can be assumed that Néel relaxation should be unchanged baring temperature variations, and the addition of Brownian contributions to heating enhancement should occur at a rate relative to a relaxation time of 3.28E-03 seconds at 90 °C. This would imply that an SAR output of approximately 11.37 to 12.64 W/g should be provided through Néel relaxation alone at a nanoparticle loading of 5 wt%. If we consider the clustering of particles in the Paraffin samples as effectively increasing the local concentration, then it is probable that the Néel contribution to heating has been reduced. However, given the comparable SAR output of the two sample types, this reduction in Néel relaxation must be met with a Brownian contribution which enhances the effective relaxation such that the SAR output matches that of the D-Sorbitol sample. Further analysis of the degree to which each mechanism contributes to the overall heating output would be a natural progression of this work.
4.5 Comparison of Nanofluid Results and Solid PCM

The oil-based samples examined in Chapter 4 were considered to have effectively inhibited Brownian relaxation due to their highly viscous nature, and this assumption was considered reasonable due to the insignificant variation in SAR between oil sample types. Although, this was not to say that Brownian relaxation ceased altogether, as there would be a finite contribution to some extent. However, through embedding the nanoparticles within solid PCMs it is far more likely that Brownian relaxation is entirely inhibited during the “Initial Slope” induction heating portion of the sample curve. This convention must necessarily be applied in the calculation of SAR to maintain consistency between PCM and nanofluid samples. With this in mind, comparing the SAR response of solid PCM samples to the Oil based nanofluids will elucidate how reasonable the assumption of Brownian inhibition was for the nanofluids. Oil-based samples at a concentration of 5 mg/ml have equivalent wt% concentrations in a range from 0.572 to 0.588, while 10 mg/ml samples have an equivalent concentration range from 1.138 to 1.169 wt%. Embedded PCM data at 1 wt% is roughly equivalent to the 10 mg/ml concentration of Oil samples and shall be the basis of comparison. The mean SAR output of 10 mg/ml oil-based samples at 217, 303, and 397 kHz was 7.77, 11.16, and 14.70 W/g. Averaging both Paraffin and D-Sorbitol 1 wt% data presented in Table 4 shows SAR outputs of 11.28, 13.20, and 15.52 W/g for AMF frequencies of 217, 303, and 397 kHz, respectively, and signifies marked similarity between the differing sample carrier mediums. At a concentration of 5 mg/ml, the mean SAR output of oil-based samples at 217, 303, and 397 kHz was 12.29, 18.38, and 20.8 W/g, respectively.
As evidenced by Table 6, the heating output of solid embedded PCM samples at a comparable concentration range to 5 mg/ml oil samples demonstrates a like SAR response across all AMF frequencies. Variations in the SAR output for all PCM/Oil sample comparisons can be attributed to the differences in nanoparticle dispersion methods and mild concentration variance. In general, all sample concentrations indicate remarkably similar mean SAR outputs across all frequencies. This result helps to verify the notion of effective Brownian inhibition in the highly viscous oil samples and lends credence to the assertion that carrier mediums with viscosities greater than 100 mPa.s do indeed result in Néel dominant heating, for particles with diameters greater than 5 nm, as put forth by Fortin et al. [18].

4.6 Chapter Bibliography


CHAPTER 5 Conclusion

5.1 Summary of Findings

This study has experimentally investigated the induction heating response of uncapped iron oxide nanoparticles dispersed in liquid and solid phase change materials (PCM) which undergo a phase change during heating. The nanoparticles utilized were determined to have a mean diameter of 14.42 nm through transition electron microscopy imagining and their phase composition was determined through x-ray diffraction and found to be magnetite, with the presence of maghemite also possible. Magnetic nanofluids were made through the sonic dispersion of the nanoparticles in concentrations of 1, 5, and 10 mg/ml in liquid carrier mediums in mixtures of water and ethylene glycol (WEG) and oil-based mixtures of a hydraulic oil and mineral oil blend (MH). These carrier fluids were characterized through their viscosity, density, and heat capacity with WEG samples providing a span of viscosities from 1.024 to 17.12 mPa.s and MH samples spanning a much higher viscosity range from 171.6 to 234 mPa.s. Experimental evaluation of the thermal response of these nanoparticles was evaluated using an alternating magnetic field with an amplitude of 72.6 kA/m at three frequencies: 217, 303, and 397 kHz. The time-temperature response of the samples was utilized in the calorimetric calculation of the specific absorption rate (SAR) which was the metric by which to compare samples. Nanofluid samples exhibited SAR attenuation with increasing concentration, and a somewhat linear SAR enhancement was found through increasing the AMF frequency. Additionally, nanofluids demonstrated continual decay with increasing carrier fluid viscosity in the WEG regime, but oil-based samples denote a reasonably consistent SAR output independent of viscosity. This result is attributed to the inhibition of Brownian relaxation in oil samples which would then rely only on Néel relaxation and hysteresis losses to generate heat. Particle aggregation in the nanofluid
samples was characterized through dynamic light scattering at concentrations ranging from 0.025 to 0.1 mg/ml. The measured effective diameter of each sample showed a consistent and significant decrease through the WEG regime from a maxima in a purely deionized water medium (WEG100) with MH samples demonstrating reasonably consistent effective diameters across the viscosity range. This data was used to develop a model to predict the Brownian contribution to heating for nanoparticles within the WEG regime through the assumption of inhibited Brownian relaxation in the MH samples.

Further analysis of this batch of nanoparticles was undertaken to characterize the SAR response in solid and liquid carrier mediums through the use of phase change materials (PCM). Investigation of the heating response in a solid phase provides a representation of the Néel and hysteresis contributions through the reasonably assumed inhibition of Brownian relaxation. Similarly, characterization of the Brownian contribution was observed through the solid to liquid phase change of the PCM which augmented the effective relaxation of the nanoparticles. The PCMs chosen for this experiment were Paraffin wax and D-Sorbitol which were characterized through their heat capacity and melting temperatures taken with a differential scanning calorimeter (DSC) with solid and liquid state values reported. Both PCMs presented two peaks in their DSC heat flow plots corresponding to minor and major phases of the material and indicate the potential for two distinct melting temperature regions. Although the bulk of the PCM corresponds to the major phase, identification of the onset melting temperature of the minor phase provided a maximum temperature in which each PCM was considered to be in a solid phase. The solid phase SAR response of the embedded nanoparticles was calorimetrically calculated at concentrations of 1, 5, and 10 wt% demonstrating SAR attenuation with increasing
concentration, similar to nanofluid samples, with little variation in SAR between PCM types at each frequency, denoting a realistic representation of Brownian excluded heating. Further investigation of solid embedded PCM samples at a comparable loading to oil-based nanofluids presented similar SAR results at each frequency, thereby certifying the assertion that Brownian relaxation is effectively inhibited in the highly viscous MH samples. Additionally, the onset of Brownian relaxation during the solid to liquid phase change of the PCM was examined with a subset of data at 217 kHz. The low viscosity of liquid phase Paraffin wax allowed for the onset of Brownian heating mechanisms with a 15.6 percent increase in SAR observed post phase change. This result is partially attributed to the onset of Brownian relaxation in liquid Paraffin which also saw significant nanoparticle settling and clustering plausibly augmenting the heating output. In contrast, the extremely viscous nature of liquid D-Sorbitol inhibited the onset of Brownian relaxation, with samples presenting a 10 percent decrease in SAR post phase change. The SAR attenuation of liquid D-Sorbitol is attributed to the visible constriction of the sample when exposed to the AMF whereby the liquid PCM is pulled down and out in the sample vial visibly augmenting its concave meniscus. This phenomenon appears to be a reminiscent of the settling of nanoparticles in liquid Paraffin, but due to the highly viscous nature of liquid D-Sorbitol the nanoparticles are unable to precipitate out of the PCM, and therefore augment the shape of the material to better align with the magnetic field. This physical constriction appears to account for the 10 percent decrease in SAR for liquid D-Sorbitol by exacerbating interparticle dipolar interactions by effectively enhancing concentration through a volume change in the sample.
5.2 Major Accomplishments

This study has expounded upon the existing research to date with exploration of many of the major factors affecting the heating output of magnetic nanoparticles. The major accomplishments of this study are as follows:

1. Experimental calorimetric characterization of the heating output of 14.42 nm iron oxide nanoparticles sonically dispersed as ferrofluids with consideration of the following factors:
   a. AMF frequency at 217, 303, and 397 kHz demonstrating SAR enhancement with increasing frequency.
   b. Nanoparticle concentration at 1, 5, and 10 mg/ml demonstrating SAR attenuation with increasing concentration.
   c. Carrier fluid viscosity for distinct mediums in low and high viscosity ranges:
      i. Six samples spanning 1.024 to 17.12 mPa.s which presented continually decreasing SAR values with increasing viscosity.
      ii. Five samples spanning 171.6 to 234 mPa.s which noted consistent and similar SAR outputs independent of viscosity indicating the cessation of Brownian relaxation.

2. Nanoparticle clustering with respect to carrier fluid viscosity demonstrated smaller effective diameters with increasing viscosity in the low viscosity range, corresponding to reductions in SAR. High viscosity samples demonstrated comparable cluster sizes across the viscous range also corresponding to trends in SAR further exhibiting SAR as a function of nanoparticle clustering.
3. Isolated the Néel and hysteresis contributions to heating through the calorimetric calculation of SAR for nanoparticles embedded in solid PCMs which inhibit Brownian relaxation. Confidence in this result is supported through the minor variance in SAR for the two sample bases, Paraffin wax and D-Sorbitol, across AMF frequencies and nanoparticle concentrations.

4. Comparison of the SAR of solid phase PCM embedded NP at comparable concentrations to the highly viscous oil blends reasonably demonstrates the cessation of Brownian relaxation in this viscosity range.

5. Evaluation of the change in SAR with the onset of Brownian relaxation during a solid to liquid phase change for liquid Paraffin demonstrates a 15.6 percent increase in SAR for liquid state Paraffin over its solid phase with liquid D-Sorbitol demonstrating a 10 percent decrease. Discussion on the factors affecting these outcomes is provided with emphasis placed on how the AMF affects the nanoparticles in each PCM.

Overall, this study presents a varied experimental approach to the thermal characterization of iron oxide nanoparticles in an alternating magnetic field with the focus placed on the physical interaction of the particles and their carrier medium. Nanofluid samples provided insight into the effects of heating output across two wide viscosity spans for varied AMF frequencies and NP concentrations with extensive analysis performed on solid PCM samples to further validate trends and provide characterization for distinct modes of heating with and without Brownian relaxation.
5.3 Conclusions and Recommendations

The research presented within this manuscript describes the varied thermal response of iron oxide nanoparticles through the modification of factors influencing the heating output. The experimental data presented quantitatively characterized the heating output of commercially available iron oxide nanoparticles and further substantiates trends associated with the induction heating of magnetic ferrofluids while also validating assertions set forth in literature through the inclusion of the induction heating results of nanoparticles dispersed in phase change materials. The latter of which validated the effective cessation of Brownian relaxation in a highly viscous environment. This study concludes that the calorimetric calculation of SAR sees attenuation with increasing carrier fluid viscosity and nanoparticle concentration while enhancing SAR with increasing AMF frequency. The observed decrease of 1.27 W/g in SAR during the solid to liquid phase change of a 5 wt% sample of D-Sorbitol at an AMF frequency of 217 kHz, attributed to the sample constricting in the AMF, further validates the notion of interparticle dipolar interactions working to reduce the heating output by stabilizing particles against the AMF. This conclusion is supported by findings of Usov et al. in their 2020 paper which indicate SAR attenuation with increasing nanoparticle cluster sized [1]. The implications of this result requires that the nanoparticle settling observed in liquid Paraffin wax would work to inhibit Néel relaxation in settled nanoparticles, meaning the observed increase of 1.54 W/g in SAR with the onset of Brownian relaxation during the solid to liquid phase change of the 5 wt% Paraffin wax samples, at an AMF frequency of 217 kHz, would actually be an underrepresentation of the total heating contribution of Brownian relaxation. The 9.90 W/g SAR value attributed to Néel relaxation and hysteresis losses would necessarily reduce with the pronounced settling and clustering of nanoparticles, however, the degree to which this would affect the SAR is unclear.
Applying this reasoning to the nanofluid samples would also indicate a lessened degree of Néel relaxation at low viscosities where nanoparticle clustering is pronounced, as indicated by the significant trend of effective diameter and viscosity. However, the assumption of Néel based attenuation with increasing cluster size stand in conflict with experimental results from Carlton et al. [2] which demonstrated SAR enhancement with increasing effective diameter. Although this was for TX-100 capped nanoparticles while the nanoparticles in this study were uncapped.

In general, research with regard to nanoparticle concentration and clustering effects tend to present disparate results from study to study. This could be attributed to differences in evaluating the linear time-temperature response (dT/dt) for the calorimetric calculation of SAR, and having a standard time interval for evaluating this term may help to clear up discrepancies in the ascribed thermal response with respect to nanoparticle concentration and clustering. For nanoparticles embedded in a solid PCM, a reasonable cap on the time-temperature response would be the first onset melting temperature, although the potential for the onset of Brownian relaxation due to localized melting is still of concern. Nonetheless, future research should further explore the effects of nanoparticle clustering with respect to the modification of SAR in nanofluids and other relevant mediums with additional consideration of pH and other factors which influence aggregation. Effort should be applied to understanding not only the effects of clustering on Néel and hysteresis losses, but also how clustering affects Brownian relaxation. It is important to quantify how the physical interaction of the nanoparticles and the carrier medium change with respect to the degree of clustering, and to recognize any potential threshold by which adequately clustered particles might inhibit particle rotation. Additionally, research into these factors should occur for capped and uncapped nanoparticles to quantify any variance that
may arise between these two particle treatments. Further investigations on the induction heating response in solid phase change materials would provide a reasonable quantitative representation of the heating output of nanoparticles which excludes Brownian relaxation. These carrier mediums offer the additional opportunity of SAR enhancement through the onset of Brownian relaxation post phase change which could be harnessed for targeted applications. Overall, the breadth of research surrounding the induction heating of nanoparticles has provided insight both qualitative and quantitative for myriad factors and treatments of both the nanoparticles themselves and the AMF in which they interact. Further efforts to characterize heating responses should be targeted at understanding trends which, to date, are conflicting in the reported literature, however, these efforts must be broadly applicable in scope. Additional focus on the effects of viscosity on heating should be investigated with emphasis on the nanoparticle clustering within these mediums.

5.4 Chapter Bibliography
