Thermorheological Properties of Nanostructured Dispersions

By

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Abstract

Nanostructured dispersions, which consist of nanometer-sized particles, tubes, sheets, or droplets that are dispersed in liquids, have exhibited substantially higher thermal conductivities over those of the liquids alone. While it is desirable to synthesize a fluid that has improved heat transfer characteristics, it is necessary that the viscosity remain low, so as not to appreciably increase the pumping power needed to employ these fluids in "real world" applications. To this end, the rheological and thermal properties of twenty-six different nanostructured dispersions were examined. In terms of rheometry, both steady flow and creep tests were employed, while the transient hot wire technique was utilized to perform measurements of the thermal conductivity of each fluid. Characterization of the dispersed phase was completed using dynamic light scattering and transmission electron microscopy. In particular, the dispersion properties examined were nanostructure material, nanoparticle size, base fluid material, nanostructure concentration, and presence of a surfactant.

It was observed that several of the fluids or nanopowders obtained from commercial manufacturers either contained no particles, had the presence of a relatively large proportion of water in ethylene glycol-based fluids, or were composed of particles with sizes far in excess of those claimed by the manufacturer. Ultimately, it was determined that while most of the fluids studied demonstrated Newtonian or slightly shear thinning behavior, several of the fluids exhibited undesirable yield stresses that could be attributed to the formation of a network structure of aggregated nanoparticles. However, it was observed that the addition of a surfactant helped to keep the nanoparticles from clustering to the same degree, thereby eliminating the presence of a yield stress, and reducing the viscosity of the fluid over the entire range of shear rates. The surfactant also contributed to an increase in thermal conductivity enhancement, thereby producing a highly desirable behavior.

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Chapter 1

Introduction and Background

The problem of cooling mechanical and electrical components has become a major obstacle in advancing new technologies. Currently, several adequate means for cooling components exist, with the utilization of fluids being one of the most common and most effective. Several examples where heat transfer fluids (HTFs) are presently employed include automotive and aerospace cooling systems in the transportation industry, heating and cooling systems in buildings, and industrial processing of goods including textiles, paper products, food, chemicals, and many others. In each of these applications, the thermal conductivity of the HTF is a crucial factor in the design of the cooling system. Therefore, with the increasing need for products to operate as efficiently as possible, companies are continuously seeking HTFs with the highest thermal conductivity and most effective cooling capacity [1].

1.1 Motivation for Improved Heat Transfer Fluids

Recent years have seen a major growth in the electronics, communications, and computing industries. With the continuous miniaturization of devices, and the exponential increase in data storage, thermal management has become a primary concern. Due to the
small size and therefore, reduced space for cooling, the emergence of nanotechnology and widespread use of Micro-Electro-Mechanical Systems (MEMS) have magnified the need for more efficient cooling methods. Miniaturized devices are not the only technologies seeking innovative cooling techniques. Larger equipment, too, is seeking innovative cooling techniques. Examples of these types of instruments include lasers, high-power x-rays, optical fibers, fuel cells, and many others. Each of these new technologies produce increased thermal loads that necessitate advances in cooling. Furthermore, the automotive industry would greatly benefit from these advances by enabling a reduction in cooling system size leading to greater fuel economy.

While extended surfaces, such as fins, are one conventional method for increasing heat transfer rates, their effectiveness has reached a limit [2]. The use of liquid coolants is another widespread method for increasing the heat transfer capability of cooling systems. However, current liquid coolants exhibit inherently poor thermal conductivities. For example, as shown in Table 1-1, the thermal conductivity, $k$, of water, a common coolant for automotive applications, is approximately 700 times less than that of copper. The thermal conductivities of other commonly used coolants such as engine oil or ethylene glycol are even lower than that of water. Therefore, it is clear that the ever-increasing power requirements and reduction in size of modern devices point to the need for improved cooling technologies [3]. One recent proposed solution by Choi, commonly denoted “nanofluids,” entails the dispersion of nanometer-sized particles with high characteristic thermal conductivities into low-thermal conductivity base fluids, in an attempt to greatly increase the overall thermal conductivity of the composite fluid [1]. The rationale behind this idea and the potential advantages of nanofluids over current HTF’s are the subject of the following section.
<table>
<thead>
<tr>
<th>Material</th>
<th>Form</th>
<th>Thermal Conductivity (W/m·K)</th>
<th>Viscosity at 25°C (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Nanotubes</td>
<td>2,000-3,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diamond</td>
<td>2,300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>110-190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fullerences</td>
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</tr>
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<td></td>
<td>Copper</td>
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<td></td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td>Nickel</td>
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</tr>
<tr>
<td>Non-Metallic Solids</td>
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<td></td>
<td>Ethylene Glycol</td>
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</tr>
<tr>
<td></td>
<td>Engine Oil</td>
<td>0.145</td>
<td>486</td>
</tr>
</tbody>
</table>

Table 1-1: Comparison of room-temperature thermal conductivity values for various solids and liquids.

1.2 Rationale Behind and Advantages of Nanofluids

The idea of suspending solid particles in liquid is not a new concept. A number of theoretical and experimental studies on the composite thermal conductivity of suspensions containing particles have been performed since Maxwell’s pioneering work more than a century ago [4]. Maxwell’s model assumes the shape of the particles to be spherical and as shown in Eq. 1.1 below, indicates that the effective thermal conductivity of the suspension increases with the volume fraction of solid particles, $\phi$. Maxwell’s effective medium theory yields the following expression for the thermal conductivity ratio,

$$\frac{k_e}{k_f} = 1 + \frac{3(\alpha - 1)\phi}{(\alpha + 2) - (\alpha - 1)\phi^3}$$

(1.1)
where \( k_e \) is the effective thermal conductivity of the composite, \( k_f \) is the thermal conductivity of the base fluid, and \( \alpha \) is the ratio of the thermal conductivity of the particle to that of the base fluid. Furthermore, it is known that increasing the surface area-to-volume ratio of the dispersed particles also enhances the effective thermal conductivity of the composite \([5]\).

For particles that have diameters smaller than 20 nm, 20% of their atoms are located on their surface \([3]\). Therefore, this allows for heat to be more effectively transferred from the particle to the surrounding liquid. This is made clear by Hamilton and Crosser \([6]\), who modified Maxwell's equation to include a dependence on the particle shape. The Hamilton-Crosser (HC) theory is given by

\[
\frac{k_e}{k_f} = \frac{\alpha + (n-1) - (n-1)(1-\alpha)\phi}{\alpha + (n-1) + (1-\alpha)\phi},
\]

where \( n \) is the empirical shape factor and is given by

\[
n = \frac{3}{\psi},
\]

where \( \psi \) is the sphericity, defined as the ratio of the surface area of a sphere with a volume equal to that of the particle, to the surface area of the particle. Another common way of quantifying the size of a particle in terms of its surface area is known as the specific surface area (SSA), which is the ratio of surface area to weight of a particle or group of particles.

The interface between two materials acts as an obstacle to heat flow because of a combination of a poor mechanical or chemical connection at the interface, and/or a difference in thermal expansion properties. While it is usually negligible for macroscopic objects, this is not the case for nanoparticles. Therefore, it is important that the interfacial resistance, or Kapitza resistance, \( R_k \), be included in thermal calculations in order to accurately predict such things as temperature distribution, heat flux, and even the thermal...
conductivity of the composite. Interfacial resistance arises from the differences in phonon spectra of the two phases, and subsequently from scattering of the phonons at the interface. Hasselman and Johnson modified Maxwell’s effective medium theory to include such a term [7]. The resulting theoretical prediction for the effective thermal conductivity enhancement of a particle-liquid dispersion is given by

\[
\frac{k_e}{k_f} = \frac{k_p(1 + 2\beta) + 2\phi[k_p(1 - \beta) - k_f]}{k_p(1 + 2\beta) + 2\phi[k_p(1 - \beta) - k_f]},
\]

where, as before, \(k_e, k_f, \) and \(\phi\) are the effective thermal conductivity of the composite, the thermal conductivity of the base fluid, and the volume fraction of particles, respectively. Also, \(k_p\) is the thermal conductivity of the particle phase, and

\[
\beta = \frac{2R_kk_f}{d},
\]

where \(d\) is the average particle diameter. In the absence of thermal boundary resistance \((R_k=0)\), Eq. 1.4 reduces to Maxwell’s effective medium theory (Eq. 1.1).

Several empirical studies have also been conducted in an attempt to increase the thermal conductivity by forming slurries of dispersed particles [8], [9]. However, all previous studies examined the use of particles whose diameters were millimeter- or micrometer-sized [5]. These types of suspensions have several disadvantages: 1) the particles quickly settle out of the carrier fluid, 2) the particles erode components through abrasive wear, 3) the particles clog narrow flow channels, and 4) with the addition of particles, the pressure drop in the fluid increases considerably [3].

The advent of nanoparticle and carbon nanotube technology sparked the reexamination of suspensions of solid particles for increasing the effective thermal conductivity of liquids. In particular, nanoparticles can differ from the parent material in terms of mechanical, thermal, electrical, and optical properties. In addition to less particle
momentum, high mobility, and increased specific heats owing to their crystalline structure [10], nanoparticles also have much larger surface areas than their millimeter- or micrometer-sized counterparts. The surface area-to-volume ratio is 1000 times larger for a particle with a diameter of 10 nm than for a particle with a diameter of 10 μm [11]. Furthermore, carbon nanotubes have been shown to exhibit thermal conductivities 20,000 times greater than that of engine oil [12].

When these nanoparticles are dispersed in carrier fluids, the resulting nanofluids exhibit several beneficial features:

1) Nanofluids are expected to demonstrate higher thermal conductivities than the base fluid due to a variety of factors. Firstly, as described above, nanoparticles have large surface area-to-volume ratios. Therefore, since heat conduction to the liquid occurs at the surface of the particles this will promote increased heat transfer. Interfacial resistance may inhibit this to some degree, but as can be seen from Eq. 1.4, thermal conductivity enhancements are still expected. Secondly, the mobility of the nanoparticles may not only increase the rate of heat transferred across a given plane through interparticle interactions, but could also induce microconvection currents which can further stimulate heat transfer. Lastly, as studies on larger particles have shown, the true enhancement in heat transfer capability is expected to be much greater than that predicted solely by thermal conductivity enhancement [8], [9], [13].

2) Because the particles are small, Brownian motion (the random thermally-driven movement of particles suspended in a fluid) can increase the stability of the suspension [14].
Whereas larger particles easily clog small flow channels, suspensions containing nanoparticles offer the potential to be used in conjunction with microchannels. This will further promote the progression towards component miniaturization by enabling the design of smaller and more efficient heat exchangers [11].

Because of their small size, nanoparticles do not carry as much momentum as their larger counterparts, and therefore will not impart nearly as much kinetic energy in collisions with mechanical surfaces. Therefore, it is expected that erosion of components will be greatly reduced. Furthermore, Hu and Dong [15] have shown that titanium oxide nanoparticles dispersed in oil reduce friction and therefore decrease wear.

Due to their large surface area-to-volume ratio, or alternatively SSA, it is expected that smaller concentrations of nanoparticles will be needed to achieve similar enhancements found for larger particle suspensions. Therefore, not only will less material be needed, but the pumping power required will also be reduced.

1.3 Objectives of Present Research

As will be discussed in Chapter 2, a wide range of studies have been published either reporting on the measurements of the thermal conductivity of nanofluids or on the theories and models that aim to accurately explain the experimental results. However, few reports address the rheology of nanofluids. This is an equally important issue, because if the
increased pumping power costs outweigh the cooling savings, the search for a new coolant is futile. This competition between viscous dissipation and heat conduction in a fluid is embodied by the Prandtl number, \( Pr \), given by,

\[
Pr = \frac{\eta c_p}{k}
\]  

where \( \eta \) is the viscosity, \( c_p \) is the specific heat capacity, and \( k \) is the thermal conductivity. Furthermore, it has been shown that while adding nanoparticles to a low-viscosity fluid increases the thermal conductivity, as indicated by Maxwell [4] in Eq. 1.1, and Hamilton and Crosser [6] in Eq. 1.2, this enhancement is also accompanied by an increase in viscosity. The viscosity of a dilute suspension of hard spheres can be predicted by the equation

\[
\eta = \eta_r (1 + 2.5\phi + 6.2\phi^2 + \ldots),
\]  

where \( \eta_r \) is the viscosity of the base fluid [16], [17], [18]. Therefore, while adding nanoparticles to a base fluid will raise the thermal conductivity, it also will increase the viscosity. For practical applications, identifying the degrees to which these two properties change is imperative.

Because of the obvious importance of maintaining a low viscosity, and subsequently reduced pumping power, the rheology of nanostructured dispersions is examined in greater detail than any previously published work. The linear rheology of the dispersions is investigated with steady shear flow and transient tests under constant stress conditions. The effects of particle loading, presence of surfactant, and preparation technique on the suspension rheology are studied. In addition, characterization (sizing and zeta potential measurements) of the suspended nanostructures is conducted via transmission electron microscopy (TEM) and dynamic light scattering (DLS).
Chapter 2

Literature Review

As was discussed in Chapter 1, nanoparticles have great potential to be more effective than millimeter- or micrometer-sized particles at increasing the thermal conductivity of fluids. This is mainly due to their small size, which increases the surface area, and promotes Brownian motion. Furthermore, the small size of nanoparticles offers them potential for use in miniaturized electronics, where larger particles would either clog the small flow channels or settle out of the carrier fluid. Lastly, recent advances in the synthesis of nanoparticles have facilitated their use on a commercial scale. This chapter will review numerous experimental studies on the thermal conductivity and viscosity of nanofluids, as well as detail the proposed theories that look to explain the sometimes anomalous experimental results.

2.1 Synthesis of Nanofluids

A large variety of possible combinations of nanoparticles, or nanotubes and base fluids, exist. Nanoparticles made from metals or metal oxides, or nanotubes in multi-walled or single-walled variations, can, with or without the help of surfactants, be dispersed into base fluids such as water, ethylene glycol, or oils. Most experimental studies synthesize nanofluids by employing what is known as a two-step process. The first step involves
creating a dry powder of nanoparticles by inert gas-condensation (IGC) [19]. This is followed by a second step in which the resulting nanoparticles are dispersed into a base fluid. The IGC process produces nanoparticles by first vaporizing the source material in a vacuum chamber, then quickly condensing the vapor into nanometer-sized crystallites via collisions with a cool, inert, low pressure atmosphere [1]. The main advantage of IGC is that it produces particles under clean conditions, without undesirable surface coatings [11]. Granqvist and Buhrman [19] utilized IGC to produce nanoparticles with diameters smaller than 3 nm. Often, agglomeration of particles occurs during the condensation phase. However, these agglomerates can easily be fractured into smaller nanoparticles using small amounts of energy [11].

A second approach to creating nanofluids is known as the one-step method, or direct-evaporation technique. This technique combines the synthesis of nanoparticles, and subsequent dispersion of the particles into a base fluid, into a single step. This approach was pioneered by Yatsuya et al. [20] and later improved by Wagener et al. [21] and Eastman et al. [5]. Like with IGC, in this process the source material is first vaporized in a vacuum. The subsequent step involves condensation of the vapor via contact with a liquid that flows continuously in order to reduce agglomeration. Agglomeration can also be suppressed by the presence of surfactants in the carrier liquid [21]. A significant advantage of this process is that it enables nanoparticles to be produced without a sometimes undesirable oxide layer which reduces the intrinsic thermal conductivity of the particles. Furthermore, the particle size produced is less than 10 nm, the distribution of particle sizes is small, and particle yield is higher than that for IGC because the evaporation rate is higher [20]. However, one critical drawback of this process is that the liquid must have a low vapor pressure, usually below 1 torr (133.3 Pa), as higher liquid vapor pressures can promote aggregation among particles.
Other relevant literature on the synthesis of nanoparticles includes a report by Enustun and Turkevich [22] on the synthesis of colloidal gold published in 1963. They detail a process which involves producing 20 nm gold particles by way of a citrate reduction. Through this process the nanoparticles are stabilized by the presence of citrate ions. Sabba and Thomas [23] utilized a solution of hydroxylamine hydrochloric acid salt to exfoliate and disperse single-walled carbon nanotubes (SWCNTs) into organic and aqueous base fluids. Furthermore, they report that this method does not break the SWCNTs or require that organic molecules be adsorbed onto the nanotube surfaces.

Another type of nanostructured suspension that does not employ the dispersion of nanoparticles is a nano-emulsion, in which nano-sized droplets of one liquid are suspended in a second liquid, and stabilized via surfactants. Porras et al. [24] studied the formation of water-in-decane nano-emulsions with various combinations of Spans® and Twesns® as surfactants. Span® and Tween® are nonionic detergents and are commonly used for emulsifying water and oils together. Droplet sizes between 30 and 120 nm were produced by vigorously stirring the water-oil-surfactant solution at 700 RPM. It is known that in order to create long-term stability in an emulsion, the strength of the interfacial film formed by a surfactant is more important than the effect of the surfactant on the interfacial tension. Furthermore, Spans® are oil-soluble, and therefore more attractive for water-in-oil emulsions because they do not settle out, but remain incorporated in the base fluid [25].

### 2.2 Heat Transfer in Nanofluids

Many experimental results have been published since Choi coined the term "nanofluid" in 1995 [1]. The main characteristics of nanofluids include thermal conductivities far in excess of those measured for conventional solid-liquid suspensions [26],
[27], [11], a strong dependence of thermal conductivity on temperature [28], [29] as well as nanoparticle concentration [30], [31], and a dependence of thermal conductivity on nanoparticle size [32], [33]. Furthermore, comparison of experimental results with existing macroscopic models, such as those developed by Maxwell [34] and Hamilton and Crosser [11], [35], points to the fact that these models are unsuitable for predicting thermal conductivities of suspensions containing nanoparticles. This is due to the fact that these models are derived from continuum-level phenomenological formulations, and therefore do not account for particle size, operating temperature, or the interface between the particles and the liquid. This section will review the numerous results reported on thermal conductivity enhancement in nanofluids, thoroughly analyze the shortcomings of current macroscopic models, and detail the work attempting to develop new theories and models to understand these anomalous experimental results. Reports on nanofluids composed of spherical oxide nanoparticle will first be discussed, followed by reports on nanofluids composed of spherical metallic nanoparticles, nanotubes, and nano-emulsions. Finally, articles detailing the theoretical analysis and modeling of the thermal conductivity of nanofluids will be reviewed.

2.2.1 Nanofluids based on Spherical Metallic-Oxide Nanoparticles

Aluminum Oxide Nanoparticles

The first report published on thermal conductivity enhancement using oxide nanoparticles in suspension was conducted by Masuda et al. [36] in 1993. By dispersing 13 nm Al₂O₃ nanoparticles in water at a volume fraction of 4.3%, they were able to obtain an enhancement in thermal conductivity of 30%. This result is corroborated by a subsequent study published by Eastman et al. [5] that also reported an enhancement of 30% for 33 nm
Figure 2-1: The ratio of nanofluid thermal conductivity to base fluid thermal conductivity was plotted as a function of Al₂O₃ concentration for (a) four different base fluids, and (b) three separate preparation methods, as reported by [37]. The Al₂O₃ nanoparticles had an average diameter of 28 nm.

Al₂O₃ nanoparticles suspended in water at a volume fraction of 5%. Pak and Cho [38] measured a thermal conductivity enhancement of 32% for a nanofluid composed of 4.33 vol.% Al₂O₃ nanoparticles in water. The volume fraction, nanoparticle size, and resulting enhancement reported in this study are almost identical to those measured by Masuda et al. [36].

Wang et al. [37] were the first to publish enhancement results of dispersing Al₂O₃ in base fluids other than water. In this work, 28 nm Al₂O₃ nanoparticles were dispersed in water, as well as ethylene glycol, engine oil, and vacuum pump oil. The results of this study are shown in Figure 2-1(a). As can be seen from the plot, the enhancements measured for the ethylene glycol- and engine oil-based nanofluids are superior to those for the water- and pump fluid-based nanofluids. The effective thermal conductivity of ethylene glycol was reported to have increased by 40% at a nanoparticle loading of 8 vol.%. The enhancement of 14% achieved by Wang et al. for Al₂O₃ nanoparticles dispersed in water at a concentration of 4.5 vol.% was far less than those reported by the previous groups even though the average diameter of nanoparticles used was similar.
Wang et al. also examined the effect of preparation technique on the thermal conductivity enhancement for Al$_2$O$_3$ nanoparticles dispersed in water. Their three preparation methods include: I) mixing the nanoparticle powder into the water using both a blending machine and an ultrasonic bath, II) repeating the first method with the addition of a polymer to coat the nanoparticles in order to decrease agglomeration, and III) filtering the nanoparticle powder to remove particles with diameters larger than 1 μm. The resulting thermal conductivity enhancements are shown in Figure 2-1(b). It can be seen that the enhancements measured for methods I and III do not differ significantly, while the addition of polymers in method II actually acts to decrease the thermal conductivity.

Lee et al. [11] measured the enhancement for 24 nm Al$_2$O$_3$ nanoparticles dispersed in both water and ethylene glycol. The water-based nanofluids showed an enhancement of about 10% at a concentration of 4.3 vol.%, and the ethylene glycol-based nanofluid showed an enhancement of about 20% at a concentration of 5 vol.%, both lower than enhancements reported previously. Das et al. [39], [28] were the first to examine the effects of temperature on thermal conductivity enhancement in nanofluids. They dispersed 38 nm Al$_2$O$_3$ nanoparticles in water at concentrations ranging from 1 to 4 vol.% and varied temperature from 21°C to 51°C. At room temperature, the enhancements measured compare well with those reported by Lee et al. [11]. However, as seen in Figure 2-2, as the temperature is increased, the enhancement also linearly increases, and depends on concentration. This trend

Xie et al. [33] examined the role of pH, thermal conductivity of the base fluid, nanoparticle size (and therefore specific surface area (SSA)) on the thermal conductivity enhancement of Al$_2$O$_3$ nanoparticles dispersed in water, ethylene glycol, and pump oil. Figure 2-3(a) shows that the thermal conductivity enhancement decreases with increased pH.
Figure 2-2: Thermal conductivity ratio as a function of temperature for two different nanoparticle concentrations, as reported by [28]. The Al₂O₃ nanoparticles had an average diameter of 38 nm, and concentrations shown are 1 and 4 vol.%. 

Furthermore, Xie et al. reported that as the thermal conductivity of the base fluid increases, the enhancement decreases. Therefore, a more dramatic enhancement will be observed for nanofluids dispersed in base fluids with lower thermal conductivities, e.g., oils. Lastly, Figure 2-3(b) points to the fact that there is a critical SSA at which the enhancement will be a maximum. This occurs for pump oil when the SSA of the Al₂O₃ particles is 30 m²g⁻¹ (60 nm...
Figure 2-4: Thermal conductivity ratio and mass diffusivity ratio as a function of \( \text{Al}_2\text{O}_3 \) concentration in water, as reported by [40]. The subscripts \( \text{nf} \) and \( \text{w} \) represent the nanofluid and water, respectively, and \( D \) is the mass diffusivity. The \( \text{Al}_2\text{O}_3 \) nanoparticles had an average diameter of 20 nm.

spherical particle), and is equal to almost 40\% at a concentration of 5 vol.\% \cite{32}. Prasher et al. found a similar trend when they measured thermal conductivity enhancement versus particle size for \( \text{Al}_2\text{O}_3 \) nanoparticles dispersed in water. They reported a maximum enhancement of 100\% at 85°C for 10 \text{nm} primary particles at a concentration of 0.5 vol.\%.

This is a surprising result, as the enhancement is far greater than previously reported by other groups, and furthermore, occurs at a much lower concentration. Furthermore, the fact that the maximum enhancement occurs at a different critical size than that reported by Xie et al. may be due to the differences in temperature between the two studies.

A more recent study by Krishnamurthy et al. \cite{40} reported on an investigation of both thermal conductivity enhancement and mass diffusivity enhancement for 20 \text{nm} \( \text{Al}_2\text{O}_3 \) nanoparticles dispersed in water. Figure 2-4 shows that while there is a peak in diffusivity enhancement at a concentration of 0.5 vol.% the thermal conductivity enhancement increases as nanoparticle concentration increases. The maximum conductivity enhancement was found to be about 16\% for a concentration of 1 vol.\%, which is higher than those reported by Wang et al. \cite{37} and Das et al. \cite{28}. 
Copper Oxide Nanoparticles

In addition to Al\textsubscript{2}O\textsubscript{3}, Eastman et al. [5] also studied the thermal conductivity enhancement of 36 nm CuO nanoparticles dispersed in water, and found that, like the Al\textsubscript{2}O\textsubscript{3} nanofluids, the enhancement increases linearly with increasing particle concentration. The enhancement due to the addition of CuO nanoparticles was measured to be approximately 60\% at a concentration of 5 vol.\%, which is significantly higher than the enhancement of 30\% measured for the Al\textsubscript{2}O\textsubscript{3} nanofluids at the same concentration. They claim that this disparity may be due to CuO having a higher intrinsic thermal conductivity than that of Al\textsubscript{2}O\textsubscript{3}. Lee et al. [11] also reported that their nanofluids containing CuO particles in both water and ethylene glycol exhibited greater enhancements than their Al\textsubscript{2}O\textsubscript{3} nanofluid counterparts. However, they attribute the difference in enhancement to nanoparticle size, as the 18.6 nm CuO nanoparticles are slightly smaller than the 24.4 nm Al\textsubscript{2}O\textsubscript{3} nanoparticles. The largest thermal conductivity enhancement that they measured was approximately 20\% at a nanoparticle concentration of 4 vol.\% in ethylene glycol.

Wang et al. [37] measured the thermal conductivity enhancement of 23 nm CuO particles dispersed in both water and ethylene glycol and found the enhancements of the water-based nanofluids to be in good comparison with the measurements reported by Lee et al., but much lower than the enhancements published by Eastman et al. Wang et al. measured conductivities at much higher concentrations than the previous two groups, and found a maximum enhancement of approximately 55\% at a concentration of almost 15 vol.\%. Das et al. [28] found that their CuO-in-water nanofluids exhibited enhancements comparable to those measured by Lee et al. and Wang et al. The average size of the CuO nanoparticles was measured to be 28.6 nm. Furthermore, Das et al. measured the thermal conductivity enhancement as a function of both temperature and nanoparticle concentration.
for temperatures ranging from 21°C to 51°C, and at concentrations of 1 vol.% and 4 vol.%. Figure 2-5 shows that, unlike the Al₂O₃ nanofluids, the rate of increase of enhancement with increasing temperature is similar between the two different concentrations, with a maximum enhancement of approximately 36% occurring at a temperature of 51°C and a concentration of 4 vol.%.

**Titanium Dioxide Nanoparticles**

Al₂O₃ and CuO nanoparticles are studied in the majority of reports published on dispersing spherical oxide nanoparticles because of their ready availability and initial success in providing considerable enhancements in thermal conductivity. However, other oxide nanoparticles, such as TiO₂, are also available. Pak and Cho [38] dispersed 27 nm TiO₂ nanoparticles into water, and measured a thermal conductivity enhancement of 10.7% at a concentration of 4.35 vol.%. This value is far less than the 32% enhancement found by the same group for Al₂O₃ nanofluids at a similar concentration.
Table 2-1 summarizes the results of the thermal conductivity enhancements reported for spherical oxide nanofluids including nanoparticle material, nanoparticle size, base fluid type, maximum nanoparticle concentration, and maximum enhancement observed.
2.2.2 Nanofluids based on Spherical Metallic Nanoparticles

Copper Nanoparticles

While fewer studies have been conducted on nanofluids containing metal nanoparticles, the results have typically been even more encouraging than those for nanofluids containing oxide nanoparticles. This is particularly the case for Cu nanoparticles, which have been reported to exhibit enhancements of approximately 45% with the addition of less than 0.055 vol.% of 35 nm particles in pump oil [5]. Metallic nanoparticles have higher intrinsic thermal conductivities than their metallic-oxide counterparts. Therefore, the concentration of nanoparticles is more than 50 times less than that required to provide a similar enhancement in a nanofluid composed of CuO in water synthesized by the same group. Xuan and Li [35] dispersed Cu nanoparticles in both water and transformer oil, and attempted to compare their results to the enhancements measured by Eastman et al. However, in comparing their copper/oil nanofluid to the nanofluid synthesized by Eastman et al., they neglected to realize that the concentration reported by Eastman’s group is 0.05 vol.% which is not the same as a volume fraction of 0.05, as depicted by Xuan and Li in
Figure 2-7: Thermal conductivity ratio as a function of concentration for three different Cu nanofluid preparations in ethylene glycol, as reported by [41]. The Cu nanoparticles had an average diameter of less than 10 nm, and were dispersed in ethylene glycol using a one-step method. Comparison is made with Al2O3/EG and CuO/EG nanofluids synthesized by the same group.

Furthermore, in order to achieve the same level of enhancement as that reported by Eastman et al., a concentration of 7.5 vol.% Cu nanoparticles dispersed in transformer oil was found to be necessary. Ultimately, the Cu nanoparticles used by Xuan and Li may not actually be pure copper, but CuO, because a two-step dispersion technique was used, which exposed the nanoparticle powder to air, creating the potential for a thin oxide layer. This is further evidenced by the strong correlation of enhancement results for their “Cu/water” nanofluid when compared with a CuO/water nanofluid system synthesized by the Eastman group, as shown in Figure 2-6(b).

Eastman et al. [41] also measured the thermal conductivity enhancement of Cu nanoparticles with an average diameter of less than 10 nm dispersed in ethylene glycol (EG). The nanofluid was produced using a one-step synthesis method. Figure 2-7 shows the resulting enhancements for three different preparations as a function of nanoparticle concentration. Maximum thermal conductivity enhancement occurs for the nanofluid stabilized by thioglycolic acid and is approximately 40% at a concentration of 0.2 vol.%.
Furthermore, fresh nanofluids that were measured within two days of preparation exhibited slightly higher enhancements than fluids that had been stored for up to two months. Lastly, as can be seen from Figure 2-7, the Cu/EG nanofluids exhibited significantly higher thermal conductivity enhancements than CuO/EG or Al₂O₃/EG nanofluids, which may be due to two potentially important differences: 1) the Cu particles have a much higher intrinsic thermal conductivity than CuO or Al₂O₃ nanoparticles, as shown in Table 1-1, and 2) the Cu particles synthesized by Eastman et al. [41] had average diameters that were much smaller than those reported for CuO or Al₂O₃ particles (~10 nm versus ~35 nm).

**Gold and Silver Nanoparticles**

Patel et al. [29] prepared gold (Au) and silver (Ag) particles via citrate reduction [22]. The Au particles had an average diameter of 10-20 nm, while the Ag particles had an average diameter of 60-80 nm. Furthermore, Au particles were also synthesized with a thiolate covering [42], and had an average diameter of 3-4 nm. As with the work of Das et al. [28] for oxide nanoparticles, the enhancement in the thermal conductivity increased with increasing temperature, as shown in Figure 2-8. Maximum enhancements occurred at a temperature of 60°C and were found to be 8.8% for Au-thiolate in toluene at a concentration of 0.011 vol.%, 8.3% for Au-citrate in water at a concentration of 0.00026 vol.%, and 4.5% for Ag-citrate in water at a concentration of 0.001 vol.%. The fact that the Ag nanofluid exhibited smaller enhancement than the Au nanofluids is surprising because Ag has a higher intrinsic thermal conductivity than gold (429 W/m·K versus 317 W/m·K), and the concentration of Ag nanoparticles dispersed in water was an order of magnitude larger than that for the gold nanofluids. Patel et al. speculate that this could be due to the Ag nanoparticles having a much larger size than the Au nanoparticles. Furthermore, the
enhancements were found to be on the same order as those obtained by Lee et al. [11] and Das et al. [28] for oxide nanoparticles, even though the concentrations of nanoparticles in the two studies ranged from 1-4 vol.%, two orders of magnitude larger than that of the Au and Ag nanoparticles used by Patel et al.

**Iron Nanoparticles**

Hong et al. [31] dispersed 10 nm Fe nanoparticles in ethylene glycol, and studied the effect of both sonication time and rest time after sonication on thermal conductivity enhancement. An ultrasonic cell disruptor generating pulses of 700 W was used. Figure 2-9(a) shows the thermal conductivity ratio versus sonication time for four different nanoparticle concentrations. Stars, triangles, circles, and squares represent 0.2, 0.3, 0.4, and 0.55 vol.%, respectively. It can be seen that the sonication acts to break up nanoparticles that have formed clusters. The nanofluids reach a constant enhancement after about 50 minutes of sonication, and the maximum enhancement is approximately 18% at a concentration of 0.55 vol.%. Figure 2-9(b) presents the average nanoparticle cluster size as a
Figure 2-9: (a) Thermal conductivity ratio versus sonication time for four different Fe nanoparticle concentrations in ethylene glycol, where stars, triangles, circles, and squares represent 0.2, 0.3, 0.4, and 0.55 vol.%, respectively. (b) Average nanoparticle cluster size is plotted versus time after sonication is stopped, for a 0.2 vol.% Fe nanofluid originally sonicated for 30 minutes. The inset shows thermal conductivity ratio versus rest time for the same nanofluid. Results reported by [31].

Figure 2-10: Thermal conductivity ratio versus concentration for 10 nm Fe nanoparticles dispersed in ethylene glycol, as reported by [31].

function of rest time after sonication for a 0.2 vol.% nanofluid. The inset plots enhancement versus rest time and shows that after 40 minutes the enhancement has become constant at a value of about 8.5%. Therefore, it is apparent that the thermal conductivity enhancement is tied directly to the degree of nanoparticle clustering. Lastly, Figure 2-10 shows that the nonlinear trend of enhancement with nanoparticle concentration may be due to more rapid clustering of nanoparticles at higher concentrations.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Nanoparticle Material</th>
<th>Reported Nanoparticle Size (nm)</th>
<th>Base Fluid</th>
<th>Maximum Concentration (vol.%)</th>
<th>Maximum k/kf at Room Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastman et al., 1997 [5]</td>
<td>Cu</td>
<td>18</td>
<td>Pump Oil</td>
<td>0.055</td>
<td>1.45</td>
</tr>
<tr>
<td>Xuan and Li, 2000 [35]</td>
<td>Cu</td>
<td>100</td>
<td>Water</td>
<td>7.5</td>
<td>1.75</td>
</tr>
<tr>
<td>Xuan and Li, 2000 [35]</td>
<td>Cu</td>
<td>100</td>
<td>Transformer Oil</td>
<td>7.5</td>
<td>1.45</td>
</tr>
<tr>
<td>Eastman et al., 2001 [41]</td>
<td>Cu</td>
<td>10</td>
<td>Ethylene Glycol</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Patel et al., 2003 [29]</td>
<td>Au</td>
<td>15</td>
<td>Toluene</td>
<td>0.011</td>
<td>1.088 @60°C</td>
</tr>
<tr>
<td>Patel et al., 2003 [29]</td>
<td>Au</td>
<td>15</td>
<td>Water</td>
<td>0.00026</td>
<td>1.083 @60°C</td>
</tr>
<tr>
<td>Patel et al., 2003 [29]</td>
<td>Ag</td>
<td>70</td>
<td>Water</td>
<td>0.001</td>
<td>1.045 @60°C</td>
</tr>
<tr>
<td>Hong et al., 2006 [31]</td>
<td>Fe</td>
<td>10</td>
<td>Ethylene Glycol</td>
<td>0.55</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 2-2: Summary of maximum measured thermal conductivity enhancements for nanofluids based on spherical metallic nanoparticles.

Table 2-2 summarizes the results of the thermal conductivity enhancements reported for nanofluids based on spherical metallic nanoparticles including nanoparticle material, nanoparticle size, base fluid type, maximum nanoparticle concentration, and maximum enhancement observed.

2.2.3 Carbon Nanotube Suspensions

Theoretical and experimental research over the past decade has pointed to the fact that carbon nanotubes can have thermal conductivities in excess of 3000 W/m·K for multi-walled carbon nanotubes (MWCNTs) [12], and 6000 W/m·K for single-walled carbon nanotubes (SWCNTs) [43]. The first reported thermal measurements performed on SWCNTs were conducted by Hone et al. [44] and involved measuring the thermal conductivity of mats or tangled bundles of tubes that had been produced by either arc-discharge or laser vaporization. The average diameter of the SWCNTs was measured to be 1.4 nm, and the thermal conductivity of the tube mat was found to be 35 W/m·K, more than two orders of magnitude smaller than that reported by Berber et al. [43]. Yi et al. [45]
and Borca-Tasciuc et al. [46] also conducted studies to measure the thermal conductivity of film arrays of MWCNTs that had been produced by chemical vapor deposition. The MWCNTs had average diameters of 20-40 nm, lengths of 1 mm, and thermal conductivities on the order of 20 W/m·K, again much smaller than previously predicted [12].

The aforementioned results demonstrate that the measured thermal conductivities are often less than expected. Possible explanations for this discrepancy include degree of tube alignment, tube quality, and tube-tube contacts. While carbon nanotubes (CNTs) have large thermal conductivities in the longitudinal direction, this is not the case for the transverse direction, for which the thermal conductivity is expected to be as low as 0.4 W/m·K, the thermal conductivity of fullerenes [47]. Therefore, since the measurements were performed on mats or bundles of randomly-oriented CNTs, the thermal conductivities will be decidedly lower than the vale expected for an ideally oriented CNT. Furthermore, an individual CNT may have defects that can act to scatter phonons. As demonstrated by Che et al. [48], a 1% vacancy concentration can act to reduce the thermal conductivity of a CNT by almost an order of magnitude. Lastly, multiple tube-tube contacts could act to decrease thermal transport due to the small contact areas between tubes which will act to scatter phonons. It can also be expected that the contact, or equivalently Kapitza, resistance between the tubes is significant. The hypothesis of tube contact reducing the overall thermal conductivity is supported by the fact that tube mats exhibit thermal conductivities much smaller than that measured for a single CNT [49].

As can be seen from the above results, CNTs can exhibit thermal conductivities an order of magnitude larger than that of copper. This, along with their low density (~0.2 g/cm³) in comparison to metals (~1-20 g/cm³), makes CNTs attractive candidates for employment in nanofluids. The most prominent report on the use of CNTs suspended in a
Figure 2-11: Thermal conductivity ratio versus concentration for MWCNTs dispersed in PAO oil, as reported by [26]. The inset represents enhancement versus concentration predicted by existing macroscopic theories: a) Hamilton-Crosser, b) Bonnecaze and Brady, and c) Maxwell.

liquid for enhanced thermal conductivity applications, was that of Choi et al. [26] who dispersed MWCNTs into a low-thermal conductivity synthetic poly-alpha-olefin (PAO) oil using a two-step method. The MWCNTs had a mean diameter of 25 nm and a length of 50 μm, and were dispersed into PAO oil at concentrations up to 1 vol.%. They were able to measure an enhancement of approximately 160% at a loading of 1 vol.%. Most surprising, however, is that even at low concentrations, the enhancement increases as a function of loading in a strong nonlinear fashion, as shown in Figure 2-11. This indicates that the interaction between individual fibers promotes increased heat transport.

Other studies involving dispersing CNTs into organic liquids or water have produced less extraordinary results. Xie et al. [50] dispersed MWCNTs in water, ethylene glycol, and decene, and measured an enhancement of approximately 20% at 1 vol.%. Wen and Ding [30] measured the enhancement of MWCNTs suspended in water as a function of both concentration and temperature. They found that below 30°C the enhancement increases linearly with increasing temperature, but that this trend levels off at temperatures in excess of 30°C. The maximum enhancement of approximately 31% was observed at a concentration of 0.84 vol.% and a temperature of 60°C. Ding et al. [51] also studied the enhancement
caused by dispersing MWCNTs in water as a function of both concentration and temperature and found that the enhancement increased with increasing temperature and concentration, with the dependence on the temperature much more noteworthy. Furthermore, as shown in Figure 2-12, at 20°C and 25°C the dependence of enhancement on concentration levels off at CNT loading above approximately 0.5 wt.%, while remaining strong for measurements performed at 30°C. The maximum enhancement achieved was approximately 80% at a concentration of 1 wt.%.

Two coauthors of the initial report by Choi et al. [26] revisited the enhancement caused by dispersing MWCNTs in PAO oil several years later. In addition to measuring the enhancement as a function of concentration, Yang et al. [52], measured the thermal conductivity enhancement as a function of surfactant concentration, ultrasonic dispersing energy, and aspect ratio. They discovered that the enhancement decreased with increasing dispersing energy, and therefore aspect ratio. This is due to the fact that sonicating the sample acts not only to break up agglomerations of CNTs, but also to shorten the lengths of the individual CNTs. This shortening has a detrimental effect on each individual tube's ability to transport heat, thereby decreasing the thermal conductivity enhancement of the
<table>
<thead>
<tr>
<th>Reference</th>
<th>CNT Type</th>
<th>Base Fluid</th>
<th>Maximum Concentration (vol.%)</th>
<th>Maximum k/kf at Room Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choi et al., 2001 [26]</td>
<td>MWCNT</td>
<td>PAO Oil</td>
<td>1</td>
<td>2.6</td>
</tr>
<tr>
<td>Xie et al., 2003 [50]</td>
<td>MWCNT</td>
<td>Water</td>
<td>1</td>
<td>1.06</td>
</tr>
<tr>
<td>Xie et al., 2003 [50]</td>
<td>MWCNT</td>
<td>Ethylene Glycol</td>
<td>1</td>
<td>1.12</td>
</tr>
<tr>
<td>Xie et al., 2003 [50]</td>
<td>MWCNT</td>
<td>Decene</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>Wen and Ding, 2004 [30]</td>
<td>MWCNT</td>
<td>Water</td>
<td>0.84</td>
<td>1.21 @60°C</td>
</tr>
<tr>
<td>Yang et al., 2006 [52]</td>
<td>MWCNT</td>
<td>PAO Oil</td>
<td>0.35</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2-3: Summary of maximum measured thermal conductivity enhancements for carbon nanotube suspensions.

suspension. Ultimately, the maximum enhancement measured by this group was reported as approximately 200% at a concentration of less than 0.35 vol.% This is a larger enhancement than that measured by Choi et al.[26], while having one-third of the concentration of MWCNTs.

Table 2-3 summarizes the results of the thermal conductivity enhancements reported for carbon nanotube suspensions including nanotube type, base fluid type, maximum nanotube concentration, and maximum enhancement observed.

2.2.4 Nano-emulsions

The only known study measuring the thermal conductivity enhancement of a nano-emulsion was conducted by Yang and Han [34], in which they dispersed nanometer-sized droplets of water in a continuous phase of FC-72, a perfluorinated liquid used for electronic cooling. Water droplets with an average diameter of 9.8 nm were created using an ultrasonic disruptor, and were stabilized with perfluorinated amphiphiles. Yang and Han found that the enhancement increased nonlinearly with increasing water concentration, and that a
maximum enhancement of 52% in the thermal conductivity could be obtained at a concentration of 12 vol.%. 

2.2.5 Theoretical Analysis and Modeling of the Thermal Conductivity of Nanofluids

The two most popular macroscopic theories that are used to attempt to predict the thermal conductivities of nanoparticle suspensions were derived by Maxwell [4], and later Hamilton and Crosser [6]. Maxwell's effective medium theory was introduced in Chapter 1, and is repeated as Eq. 2.1. We can see that this equation only incorporates the thermal

\[
\frac{k_e}{k_f} = 1 + \frac{3(\alpha - 1)\phi}{(\alpha + 2) - (\alpha - 1)\phi},
\]

conductivities of the two phases and the concentration of the particulate phase, and fails to include the effect of particle size or shape on the resulting thermal conductivity. The Hamilton-Crosser (HC) theory, also introduced in Chapter 1 and repeated as Eq. 2.2, aims to improve on Maxwell's work by including a particle shape factor. If Eq. 2.2 is examined

\[
\frac{k_e}{k_f} = \frac{\alpha + (n - 1) - (n - 1)(1 - \alpha)\phi}{\alpha + (n - 1) + (1 - \alpha)\phi},
\]
closely, it can be seen that when the particle phase has a thermal conductivity equal to or greater than ten times that of the base fluid, the predicted enhancement is close to the limiting value, and a further increase in the thermal conductivity of the particle phase has little effect on the enhancement. This is due to the fact that as \(\alpha\) is increased by a significant amount (10 times or more) the particles tend to have a constant temperature across their length, causing the boundary conditions at the fluid/particle interface to remain constant. Since the nanoparticles employed in nanofluids have thermal conductivities far in
excess of the base fluids they are dispersed in, Eq. 2.2 is essentially independent of particle composition. As the experimental results showed, this is clearly not the case [53].

Even though the HC theory includes the shape of the dispersed particles, it still does not include a dependence on the interface between the particles and liquid, the size of the particles, or operating temperature, which as Putra et al. [54], Das et al. [28], Ding et al. [51], and others have shown, is an important factor. Furthermore, the Maxwell and HC models assume diffusive heat transport for both the particles and the fluid and they fail to take particle mobility into account. Lastly, as Figure 2-11 shows, these macroscopic theories vastly under-predict the enhancement seen by dispersing nanoparticles or CNTs in a base fluid. Ultimately, there is a need for a more detailed, atomic-level understanding of the mechanisms that contribute to the anomalous enhancements reported, as well as a versatile model that can accurately predict the behavior of nanofluids. The next section will detail five factors that could be responsible for the inadequacy of the aforementioned macroscopic models: 1) interfacial (Kapitza) resistance, 2) molecular-level layering of the liquid at the liquid/particle interface, 3) the Brownian motion of nanoparticles, 4) the effects of clustering of nanoparticles, and 5) the nature of heat transport in nanoparticles and in particular whether it is diffusive or ballistic.

**Interfacial (Kapitza) Resistance**

As discussed in Chapter 1, the interface between two materials acts as an obstacle to heat flow because of a combination of a poor mechanical or chemical connection at the interface, and/or a difference in thermal expansion properties. Therefore, it is important that the interfacial resistance, or Kapitza resistance, $R_k$, be included in thermal calculations in order to accurately predict such things as temperature distribution, heat flux, and even the thermal conductivity of the composite. Interfacial resistance arises from the differences in
phonon spectra of the two phases, and subsequently from scattering of the phonons at the interface. The heat flux, $Q$, is related to the temperature drop at the interface, $\Delta T$, by

$$Q = G\Delta T,$$

where $G$ is the interfacial conductance, defined as

$$G = \frac{1}{R_x}.$$

The relative importance of the interfacial resistance can be quantified by an equivalent length, $b$, defined as the length over which the drop in temperature is equal to that at the interface, and is calculated by

$$b = \frac{k}{G},$$

where $k$ is the bulk thermal conductivity [2]. While for solid/solid contact between large grain-sized materials the interfacial resistance is usually negligible, for solid/liquid interfaces, this resistance depends on the properties of the adsorbed layer of liquid [55]. For macroscopic objects, it is usually still small. However, for objects such as nanoparticles or nanotubes, whose length-scales are on the order of that of an atom, the interfacial resistance becomes important in terms of overall heat transfer [56]. This is because $b$ becomes comparable to the size of the nanoparticle, or interparticle distance. Huxtable et al. [57] measured the interfacial conductance between carbon nanotubes and surfactant micelle and found it to be 12 MW/m$^2$K, which corresponds to a value of $b$ of approximately 10 nm for a typical low-conductivity organic liquid. Therefore, because this length is on the same order as that of nanoparticles or nanotubes, it is apparent that the thermal resistance should be included when analyzing nanoscale materials.

In view of the obvious significance of the thermal boundary resistance between the nanoparticle and the base fluid it is dispersed in, Hasselman and Johnson modified
Maxwell’s effective medium theory to include such a term [7]. The resulting theoretical prediction for the effective thermal conductivity enhancement of a particle-liquid dispersion, originally given in Chapter 1, is repeated as Eq. 2.6.

\[
\frac{k_e}{k} = \frac{k_p (1 + 2\beta) + 2k_f + 2\phi[k_p(1 - \beta) - k_f]}{k_p (1 + 2\beta) + 2k_f - \phi[k_p(1 - \beta) - k_f]},
\]

(2.6)

The Kapitza resistance between a particle and water can be assumed to be \( R_k = 7.7 \times 10^{-9} \) Km²W⁻¹, and it can be estimated as \( R_k = 1.2 \times 10^{-8} \) Km²W⁻¹ for a particle dispersed in ethylene glycol [58], [59].

Ultimately, however, it is obvious that inclusion of the interfacial resistance in current models would only lead to a decrease in the predicted enhancement as the particle size is reduced, which is contrary to what has been observed experimentally. Therefore, it is necessary to examine other possible causes for the discrepancy between the experimental results and existing theories.

**Liquid Layering at the Nanoparticle/Fluid Interface**

Unlike Kapitza resistance, liquid layering at the solid interface could promote heat transport from the liquid to the solid phase and vice versa. Liquid layering occurs when the atomic structure of the liquid molecules becomes more ordered than that of the bulk fluid, as depicted in Figure 2-13. Since crystalline solids, with thermal conductivities orders of magnitude higher than most liquids, exhibit ordered behavior, this liquid layer phenomenon would be expected to increase the heat transport, and therefore, the thermal conductivity of the composite. An upper limit of the effect of this liquid layering on the composite thermal conductivity can be determined by assuming that the thermal conductivity of this interfacial liquid is equal to that of the solid. Therefore, as Keblinski et al. [53] show in Figure 2-14, the thermal conductivity of a nanofluid is enhanced by the larger effective volume of the
Figure 2-13: Schematic cross section of nanofluid structure consisting of nanoparticles, bulk liquid, and ordered liquid layering at the solid/liquid interface, as reported by [60].

Figure 2-14: Thermal conductivity ratio versus nanoparticle diameter for four different liquid layer thicknesses, as reported by [53].

particle/interfacial layer structure, with the liquid layer having more of an effect as the particle size decreases. In this figure, the excess thermal conductivity enhancement, $\kappa$ is defined as

$$\kappa = \frac{k_{\text{eff}} - k_f}{k_{\text{HC}} - k_f},$$  

(2.8)
where $k_f$ is the thermal conductivity of the nanofluid, $k_n$ is the thermal conductivity of the base fluid, and $k_{HC}$ is the thermal conductivity predicted by the Hamilton-Crosser theory.

By modeling the nanoparticle and liquid layer as a complex nanoparticle, Xue [61] was able to design a new model for calculating the thermal conductivity of nanofluids. Xue compared his model with experimental results that reported on the enhancements produced by dispersing CNTs and $\text{Al}_2\text{O}_3$ nanoparticles in liquids, and found that the theory and experiments were in good agreement for a liquid layer thickness of 3 nm and a thermal conductivity an order of magnitude larger than that of the base fluid. Furthermore, he concluded that increasing the thermal conductivity of the liquid layer increases the thermal conduction from the liquid to the particle, and that for thicker liquid layers, the phonon scattering interface is larger, making heat conduction more effective.

Yu and Choi conducted a similar analysis in which they modified both the Maxwell equation [60] and the Hamilton-Crosser model [62] to include the effect of an ordered liquid layer. Like Xue, they predicted that the interfacial layer has a thickness of approximately 3 nm. Unlike Xue, however, Yu and Choi [62] found that for nonspherical particles dispersed in liquids, increasing the thickness of the ordered liquid layer will increase the sphericity of the individual particles, thereby reducing the predicted thermal conductivity of the composite. Ultimately, however, simulations [63] and experiments [64] have pointed to the fact that the liquid layer may have a thickness of less than 1 nm.

Xie et al. [65] also explored the effect of the interfacial liquid layer on thermal conductivity enhancement by modeling this ordered layer as having a linear variation in thermal conductivity; it is equal to the conductivity of the particle at the inner surface, but identical to that of the bulk fluid at its outer surface. By comparing their model to experimental data, they found that for an interfacial layer thickness of 2 nm there was good
agreement. However, they were unable to accurately predict such anomalous results as those reported by Eastman et al. [41] in which the Eastman group measured a thermal conductivity enhancement of 40% for a nanofluid containing 0.3 vol.% Cu nanoparticles in ethylene glycol. Lastly, by allowing the ordered liquid layer to have a constant thermal conductivity, instead of one that varied linearly, Xie et al. were able to predict thermal conductivity enhancements consistent with those calculated by Yu and Choi [60]. In conclusion, although it looks as if the liquid layer plays a part in thermal conductivity enhancement, it is not likely that it is solely responsible for the anomalous enhancements measured experimentally.

**Nanoparticle Motion**

Because of their small size, nanoparticles exhibit Brownian motion when dispersed in liquids. This Brownian motion, either by causing nanoparticle-nanoparticle contact or by transporting heat, can produce an enhancement in the thermal conductivity of the composite. This idea is further supported by the fact that Putnam et al. [66] found that for a polymer-nanoparticle nanocomposite, in which there was no nanoparticle motion, no enhancement in thermal conductivity was observed. However, for Brownian motion to be a considerable contributor to thermal conductivity enhancement in nanofluids, it would have to be more effective than thermal diffusion in transferring heat. However, Keblinski et al. [53] demonstrated that in a fluid, it takes $t_d = 2 \times 10^{-7}$ seconds for a 10 nm particle to move a distance equivalent to its size, while it only takes heat $t_H = 4 \times 10^{-10}$ seconds to move through the same distance. Therefore, they conclude that because thermal diffusion is markedly quicker than Brownian diffusion, it is unlikely that Brownian motion will significantly enhance the thermal conductivity of a composite. Furthermore, they demonstrated via
molecular dynamics simulations, that the flow of heat in model nanofluids was independent of whether or not the nanoparticles were allowed to move.

Krishnamurthy et al. [40] and Prasher et al. [59] came to the same conclusion as Keblinski et al. by performing a similar analysis. However, they hypothesized that enhancement in heat transport may be due to convection caused by the currents induced by the motion of nanoparticles. In particular, Krishnamurthy et al. calculated that the time required for these convection currents to travel the distance equal to a particle's diameter, $t_C$, was much less than both $t_D$ and $t_H$. On the contrary, Wang et al. [37] concluded that the heat transferred via advection of a nanoparticle was less than that transferred by diffusion, and that therefore, Brownian motion can not fully explain the enhancements realized in experiments.

The interparticle forces that exist in a nanofluid are also thought to be a possible explanation for the unusual enhancements found. In an attempt to accurately model the enhancements found, Bhattacharya et al. [67] performed a Brownian dynamics simulation that included interparticle forces. Figure 2-15 compares the results of this model with those measured via experiments, as well as with the Hamilton-Crosser model, which assumes stationary particles. It can be seen that the simulation results are within 3% of the experimental data for both Cu and Al$_2$O$_3$ nanoparticles dispersed in ethylene glycol. By employing an order-of-magnitude analysis, Prasher et al. [59], however, came to the conclusion that enhancement due to interparticle forces is negligible because of the dilute concentrations of nanoparticles in nanofluids.

Lastly, it is possible that the thermal gradients induced by the thermal conductivity measurement apparatuses could lead to motion of the nanoparticles, and ultimately, a non-uniform dispersion of nanoparticles in a nanofluid. This effect, known as thermophoresis,
could potentially effect the measurement of the thermal transport properties of a nanofluid [68], [69]. However, a detailed analysis of the effect of thermophoresis on the thermal conductivity enhancement in nanofluids has yet to be made. In conclusion, it is hypothesized that Brownian motion could contribute to nanoparticle clustering and aggregation, the subject of the following section. As will be discussed, nanoparticle clustering may be largely responsible for the thermal conductivity enhancements measured in nanofluids.

**Nanoparticle Clustering**

It is postulated that the anomalous enhancements measured in nanofluids could at least in-part be due to nanoparticles clustering or forming percolating networks. The reasoning behind this line of thinking is that these networks could form paths of decreased thermal resistance, thereby making heat transport more effective. However, because large particles tend to rapidly settle out of liquids, it is unlikely that the agglomerations could extend over long enough length-scales to have a substantial effect [53]. Furthermore, while
the percolation threshold for dispersions of particles is approximately 15 vol.%[2], unexpected enhancements have been reported for concentrations lower than 1 vol.%. Therefore, while percolating structures seem unfeasible, local nanoparticle clustering could still contribute to thermal conductivity enhancements by increasing the effective volume fraction of the nanoparticle phase. According to Hamilton and Crosser [6], by increasing the effective volume, the volume fraction of the high-conductivity phase becomes larger than the volume fraction of the primary nanoparticles, and therefore, the thermal conductivity of the composite is significantly increased. Figure 2-16 illustrates this phenomenon, by plotting the excess thermal conductivity enhancement, $\kappa'$, versus $\phi$, the packing fraction of the cluster. The packing fraction is defined as the ratio of the solid particles in the cluster to the total effective volume of the cluster. As can be seen from the figure, as the packing fraction is decreased, the effective volume increases, thereby increasing the thermal conductivity enhancement.

Keblinski et al. [53] further hypothesize that the particles in a cluster do not actually have to be in physical contact, as depicted in Figure 2-16(iv). Instead, the nanoparticles can be separated by a liquid layer with a thickness less than the phonon mean free path ($\sim 1$-2
Aggregated nanoparticles (Eq. 12 and 13)...

Well dispersed nanoparticles using M-G model

Completely dispersed

1 35

Increasing level of aggregation

0.2 0.4 0.6 0.8 1.0

$\phi_p$ (volume fraction of primary particle in the aggregate)

Figure 2-17: Thermal conductivity ratio versus degree of aggregation for a volume fraction of 0.05, as reported by [32]. $\phi_p$ is the volume fraction of primary particles in the nanofluid.

Wang et al. [70] analyzed the effects of nanoparticle clustering on the thermal conductivity enhancement in a nanofluid. By considering the fractal properties of the agglomerates, they were able to accurately predict the enhancements for nanofluids containing oxide nanoparticles, but were unable to do the same for metallic nanoparticles. Furthermore, Wen and Ding [30] speculate that the anomalous enhancements measured for CNT suspensions may be due to nanotube clustering or networking, which can create more efficient paths for ballistic heat transport.

Prasher et al. [32] improved on their previous model, which included microconvection caused by Brownian motion [59], by also taking into account the enhancement caused by nanoparticle clustering. As shown in Figure 2-17, they found that there was a critical value of the degree of aggregation for which the maximum enhancement
was realized. The Maxwell-Garnett (M-G) theory (see Appendix), on the other hand, merely predicts an enhancement independent of the degree of aggregation of nanoparticles in a nanofluid.

**Ballistic Heat Transport**

The existing macroscopic models, such as those derived by Maxwell [4] and Hamilton and Crosser [6] were designed for larger particles. Therefore, they assumed that the particles would have dimensions much larger than the phonon mean free path, thereby entailing diffusive heat transport. However, when the particles are smaller than the mean free path, heat transport is at least partially ballistic [71]. For example, the mean free path in a typical nanoparticle, such as Al₂O₃, is approximately 35 nm. Therefore, when these particles have diameters on the order of 10 nm, heat must move ballistically across the nanoparticle. Furthermore, because the phonon mean free path in a CNT is large, heat is transported ballistically [26].

However, Keblinski et al. [53] articulate that it shouldn’t matter whether heat is transported by ballistic or fast-diffusive means, because in both cases the temperature of the particle will essentially be constant, in effect causing the same boundary conditions at the solid/liquid interface. Ultimately, as discussed in the previous section, for loosely clustering nanoparticles in which the particles are separated by thin layers of liquid, ballistic heat transport can facilitate the transfer of heat from particle to particle more effectively than diffuse heat transport, thereby increasing the thermal conductivity of the composite.

While most of the studies of nanofluids to date have revolved around the measurement of thermal conductivity enhancement, few have examined an equally important property, viscosity. Gosselin and da Silva [72] have shown via a mathematical
model, that because solid/liquid mixtures are more costly to pump than the base fluid itself, there is a clear trade-off between thermal heat transfer enhancement and pumping power required. Therefore, this competition exhibits the fact that there is the ability to maximize the gains in heat transfer properties, while keeping the pumping power constant, by dispersing an optimal concentration of particles. The results of this analysis are shown in Figure 2-18, for which \( \Omega \) is the ratio of the heat transfer rate of the nanofluid to the heat transfer rate of the base fluid for laminar forced convection flow, all for a constant pumping power, and is defined as

\[
\Omega_{\text{fc, lam}}(\phi, n) = \frac{\bar{Q}^{2/3}(n, \phi) \rho_{\text{eff}}^{2/5}(\phi) c_{\text{p, eff}}^{1/3}(\phi)}{\bar{\mu}_{\text{eff}}^{4/15}(\phi)},
\]

where

\[
\bar{\mu}_{\text{eff}} = \frac{\mu_{\text{eff}}}{\mu_f} = \frac{1}{(1 - \phi)^{5/2}},
\]

\[
\bar{c}_{\text{p, eff}} = \frac{c_{\text{p, eff}}}{c_{p,f}} = (1 - \phi) + \phi \bar{c}_p,
\]

Figure 2-18: The dimensionless heat transfer rate for laminar forced convection flow versus nanoparticle volume fraction as a function of seven different shape factors, as reported by [72]. The solid and liquid properties represented are for Al\(_2\)O\(_3\) and water, respectively.
eff and \( f \) refer, respectively, to the effective and fluid properties, \( n \) is the empirical shape factor as given by Eq. 1.3, \( \phi \) is the volume fraction of nanoparticles, \( k \) is the thermal conductivity, \( \rho \) is the density, \( c_p \) is the specific heat capacity, and \( \mu \) is the viscosity. The plot shown is for solid and liquid properties of \( \text{Al}_2\text{O}_3 \) and water, respectively, and points to the fact that there is indeed a critical volume fraction at which the heat transfer rate is maximized. This critical concentration differs depending on the shape factor of dispersed particles, increases with shape factor, and reaches a constant value at \( n \geq 3 \). Furthermore, the maximum heat transfer rate also increases with increasing shape factor, indicating that the most effective nanofluids are those in which the nanoparticles are less spherical, such as CNTs. Lastly, when the volume fraction of nanoparticles reaches 1.0, the viscosity becomes so great that flow ceases, and the heat transfer rate tends to zero. In conclusion, in studying nanofluids, it is evident that while the heat transfer properties of a nanofluid be examined, it is a necessity that the rheological properties also be investigated. If the increased pumping power costs outweigh the cooling savings, the search for a new coolant is futile.

2.3 Rheology of Nanofluids

While the rheology of nanofluids has received much less attention than the heat transfer properties, the rheology of particulate dispersions has been studied for decades,
dating back to Einstein in 1906 [16]. Einstein calculated that the viscosity, \( \eta \), of a suspension of hard spheres is predicted by the equation

\[
\eta = \eta_s (1 + 2.5 \phi), \tag{2.14}
\]

where \( \eta_s \) is the viscosity of the base fluid, and \( \phi \) is the volume fraction of dispersed particles [17]. This equation, however, is only accurate at low volume fractions (\( \phi \leq 0.03 \)) when the flow around one sphere is not significantly affected by the proximity of a neighboring sphere. When two spheres are close enough so that this condition is not met, the spheres experience hydrodynamic interactions, which lead to a dependence of viscosity on concentration that is proportional to \( \phi^2 \). Analogously, interactions between \( n \) neighboring spheres entail a dependence that is proportional to \( \phi^n \) [73]. The effect on viscosity of the hydrodynamic interaction between the two spheres was studied by Batchelor in 1976 [18], in which he calculated that the proportionality constant in front of the \( \phi^2 \) term is equal to 6.2. Combining this result with Einstein’s prediction (Eq. 2.14), gives

\[
\eta = \eta_s (1 + 2.5 \phi + 6.2 \phi^2), \tag{2.15}
\]

and enables the viscosity to be accurately calculated for concentrations up to approximately 10 vol.%.

Bossis and Brady [74] show that for a suspension of spherical Brownian particles, the viscosity exhibits several different behaviors at varying shear rates, or equivalently, Peclet numbers. Figure 2-19 plots the results of their simulation as relative viscosity, \( \eta_r \), versus Peclet number, \( Pe \), where the relative viscosity is the ratio of the viscosity of the fluid with the Brownian particles, to that of the fluid without the particles. The Peclet number is defined as
Figure 2-19: Relative viscosity as a function of Peclet number for Brownian spheres dispersed in a fluid medium, as reported by [74].

\[
P_{e} = \frac{6 \pi \eta a^{3} \gamma}{kT},
\]

(2.16)

where \( a \) is the particle radius, \( \gamma \) is the shear rate, \( k \) is the Boltzmann constant, and \( T \) is the temperature. As can be seen from Figure 2-19, the total viscosity curve can be divided into three different regions: a shear thinning region at low shear rates, followed by a region in which the viscosity remains essentially constant, ultimately followed by a shear thickening region at high shear rates. Furthermore, Figure 2-19 plots the contributions of the Brownian and hydrodynamic viscosities as a function of Peclet number. The Brownian viscosity decreases rapidly at a Peclet number of approximately 0.1, causing the observed shear thinning region in the total viscosity curve. The hydrodynamic viscosity exhibits a dissimilar trend, increasing at a Peclet number of 1.0, and is responsible for the shear thickening region in the total viscosity curve. The interplay between these two viscosities creates the unique curve that is observed for many particulate suspensions.
2.3.1 Spherical Nanoparticle Suspensions

**Aluminum Oxide Nanoparticles**

In addition to being one of the first groups to measure the thermal conductivity enhancement in nanofluids, Pak and Cho [38] were also one of the first groups to measure the viscosity of nanofluids as a function of shear rate and concentration. As mentioned previously, 13 nm Al₂O₃ nanoparticles were dispersed in water at concentrations up to 10 vol.%. Figure 2-20 shows the results of the viscosity measurements as both a function of shear rate as well as nanoparticle concentration. From Figure 2-20(a) it can be observed that the nanofluids appear to exhibit Newtonian behavior (the viscosity is independent of shear rate). In Figure 2-20(b), it can be seen that the viscosity of the nanofluid was measured to be up to 300 times greater than that of the base fluid. Furthermore, the viscosities measured are in excess of those predicted by Batchelor using Eq. 2.15, and may be due to the irregular and rough shape of the dispersed particles [38]. In contrast, Wang et al. [37] measured an increase in viscosity of only 90% for similar concentrations and particle size.
Das et al. [39] also measured the viscosity of Al₂O₃ nanoparticles dispersed in water, and found that as a function of shear rate, the nanofluids exhibited similar trends to those reported by Pak and Cho. Furthermore, they conducted the viscosity measurements at three different temperatures: 20°C, 40°C, and 60°C. The results of these measurements are shown in Figure 2-21. As with the results of Pak and Cho, these nanofluids exhibited Newtonian behavior, and as expected, the maximum viscosities were recorded for the nanofluid with the greatest nanoparticle loading and lowest temperature.

Lastly, Tseng and Wu [75] conducted a more involved analysis of the rheology of nanofluids composed of 37 nm Al₂O₃ nanoparticles dispersed in water at pH values of 2 and 11. Figure 2-22 plots the results of this study as viscosity versus shear rate for volume fractions of 0.03, 0.06, 0.11, and 0.16, as well as the two different pH values. The results show that at lower shear rates the dispersions exhibit a shear thinning behavior, while at higher shear rates the behavior becomes shear thickening. Tseng and Wu hypothesize that

Figure 2-21: Viscosity versus shear rate for Al₂O₃/water nanofluids at concentrations of 1 and 4 vol.% and temperatures of 20°C, 40°C, and 60°C, as reported by [39].
the shear thinning behavior may be due to the break up of agglomerates that had existed in the fluid. This break up leads to smaller particles that are better dispersed and have lower interparticle interactions, thereby entailing a decrease in viscosity. Furthermore, the transition from shear thinning to shear thickening is abrupt and is dependent on the concentration of the nanofluid. Lastly, as can be seen from the plots, the nanofluid at a pH of 11 exhibits much higher viscosities than the nanofluid at a pH of 2, and can be attributed to the fact that at the higher pH value, the nanoparticles were less well-dispersed, and therefore, larger clusters existed. These large clusters act to increase the effective volume fraction and/or interparticle interactions, leading to an increase in viscosity.

**Copper Oxide Nanoparticles**

Kwak and Kim [27] conducted viscosity measurements on nanofluids composed of 12 nm CuO particles dispersed in ethylene glycol, and found that as the concentration is increased, the viscosity versus shear rate trend changes from being Newtonian to being shear thinning. As shown in Figure 2-23, at the highest concentration, the viscosity decreases by two orders of magnitude as the shear rate is increased from 0.01 sec\(^{-1}\) to 1000 sec\(^{-1}\).

Kulkarni et al. [76] also studied the rheology of nanofluids containing CuO nanoparticles. This time the CuO particles were dispersed in water and the viscosity was
Figure 2-23: Viscosity versus shear rate for five concentrations of CuO nanoparticles dispersed in EG, as reported by [27].

Figure 2-24: (a) Viscosity versus shear rate for a nanofluid composed of 15 vol.% CuO dispersed in water at ten different temperatures. (b) Viscosity versus CuO nanoparticle concentration at ten different temperatures. Reported by [76].

measured at ten different temperatures. Figure 2-24(a) plots viscosity versus shear rate for a 15 vol.% CuO nanofluid at ten temperatures ranging from 278K to 323K. As can be seen, the nanofluids exhibit shear thinning behavior with the degree of shear thinning dependent on the temperature; more shear thinning was observed at lower temperatures. Furthermore, as expected, the viscosities of the nanofluids decrease with increasing temperature. Figure 2-24(b) plots viscosity versus nanoparticle concentration and demonstrates the fact that there is a nonlinear increase in viscosity with increasing nanoparticle loading. This effect is reduced as the operating temperature is increased.
2.3.2 Carbon Nanotube Suspensions

Ding et al. [51] measured the viscosity of dispersions of MWCNTs in water as a function of both shear rate and temperature, and found similar results to those for spherical nanoparticle suspensions. However, as shown in Figure 2-25, the shear thinning behavior of these nanofluids was more dramatic than that for the spherical-particle nanofluids, as the viscosity decreased by more than four orders of magnitude over a range of shear rates from 0.1 sec\(^{-1}\) to 1000 sec\(^{-1}\). Furthermore, as with the studies conducted on spherical nanoparticles, the viscosity increased with greater CNT loading and decreased operating temperature.

Yang et al. [52] also studied the rheological properties of MWCNT dispersions. However, this time PAO oil was the base fluid of choice, and the effect of surfactant concentration and dispersing energy were examined. Figure 2-26(a) plots viscosity versus surfactant concentration at a shear stress of 0.07 Pa, and points to the fact that there is a minimum viscosity achieved at an intermediate concentration of 3.0 wt.% . As the loading of surfactants is increased or decreased, the viscosity increases. Figure 2-26(b), on the other hand, shows that the viscosity decreases with increasing dispersing energy up to a value of
approximately $7.2 \times 10^5 \text{ kJ/m}^3$, at which point the viscosity essentially remains constant. Yang et al. attribute this behavior to the fact that as the dispersing energy is increased, the network structure of CNTs is broken up causing a sharp decrease in the measured viscosity. Furthermore, Yang et al. found that, as with the above study conducted by Ding et al., there is an increasing trend between viscosity and CNT loading, with the degree of shear thinning largely dependent on the CNT concentration.

Davis et al. [77] found similar results in terms of the shear thinning behavior of CNT dispersions. However, instead of the nanofluids exhibiting an increasing trend of viscosity with CNT concentration, a maximum and minimum were present, as shown in Figure 2-27(a). The explanation for this phenomenon is made clear by the schematic shown in Figure
2.27(b), which demonstrates that as the volume fraction of Brownian rods, or analogously CNTs, increases, the system transitions from a dilute regime in which the rods do not interact with each other, to a liquid crystalline phase. Therefore, as the concentration increases, interactions between nanotubes inhibit motion, causing an increase in viscosity. The transition from a biphasic system to a solely liquid crystalline system occurs between the maximum and minimum in Figure 2-27(a), and if the concentration is further increased, the viscosity will continue to grow rapidly.

2.3.3 Emulsions

Pal [78] conducted an extensive study on the rheological properties of water-in-oil emulsions and found that the viscosity of fine emulsions (smaller droplet size) was greater
than that of coarse emulsions (larger droplet size), as shown in Figure 2-28. As can be seen from the plots, for all three water volume fractions, the viscosity of the fine emulsion is greater than that of the corresponding coarse emulsion. Furthermore, the shear thinning behavior is more prominent for fine emulsions compared to their coarse emulsion counterparts. Pal hypothesizes that these interesting results could be attributed to three factors: 1) as the droplet size is decreased, the separation between droplets is reduced, leading to an increase in the hydrodynamic interactions between droplets, and therefore an increase in viscosity; 2) the thickness of the adsorbed surfactant layer becomes more important as the droplet size is decreased, leading to an increase in the effective dispersed-phase concentration; and 3) the polydispersity decreases with the reduction in droplet size, and since there is a strong correlation between degree of polydispersity and viscosity (the viscosity decreases as the emulsion becomes more polydisperse) this entails an increase in viscosity. Furthermore, Pal speculates that the observed shear thinning behavior could be caused by the increased tendency of droplets to flocculate as their size is reduced. Essentially, the droplets could aggregate into a network structure of thin liquid films, inducing shear thinning.

2.3.4 Theoretical Analysis and Modeling of the Rheology of Nanofluids

While the Einstein-Batchelor correlation (Eq. 2.15) is well accepted for predicting the viscosity of a suspension of semi-dilute spherical particles, an accurate correlation that also includes the effect of operating temperature is less well-known. Kulkarni et al. [76] applied the correlation given by White [79] to their data and found good agreement. This correlation is
Figure 2-29: (a) Ratio of nanofluid viscosity to base fluid viscosity versus nanoparticle concentration in both water and EG for a Brownian dynamics simulation. Comparison to experimental results is made. (b) Ratio of thermal conductivity enhancement to viscosity enhancement versus nanoparticle concentration in water for four different average nanoparticle sizes. Results reported by [80].

\[
\ln \frac{\mu}{\mu_0} \approx a + b \left( \frac{T_0}{T} \right) + c \left( \frac{T_0}{T} \right)^2 ,
\]

where \( \mu \) is the viscosity of the suspension, \( T \) is the operating temperature, \( \mu_0 \) and \( T_0 \) are reference values, and \( a, b, \) and \( c \) are dimensionless curve fit values. Kulkarni et al. also utilized a more robust correlation that did not require the proportionality constants to be estimated through a curve fit, but instead allows them to be calculated from the volume fraction of dispersed particles. This correlation is given as

\[
\ln \mu = A \left( \frac{1}{T} \right) - B
\]

\[A = 20587\phi^2 + 15857\phi + 1078.3 \]

\[B = -107.12\phi^2 + 53.548\phi + 2.8715 \]

In addition to the mathematical model of Gosselin and da Silva [72] that was described earlier, Phelan et al. [80] have also sought to model the rheological behavior of nanofluids, as well as detail its importance in terms of designing an effective coolant fluid. Figure 2-29(a) plots the results of their Brownian dynamics simulation for a nanofluid
consisting of 28 nm Al$_2$O$_3$ particles dispersed in water and ethylene glycol and compares it to the experimental results obtained by Wang et al. [37]. As can be seen, the simulation is in good agreement with the experimental results. Figure 2-29(b) plots the results of this model as the ratio of thermal conductivity enhancement to viscosity enhancement as a function of nanoparticle loading for four different nanoparticle sizes. From the results it can be concluded that the enhancement in thermal conductivity should be greater than the enhancement in viscosity for particles whose average diameter is less than 30 nm. As the diameter is further decreased, this model predicts that greater enhancements will be realized.
Chapter 3
Experimental Methods

3.1 Nanofluid Preparation and Dilution Techniques

In the next two chapters, the results of the examination of a series of nanofluids are discussed. The types of nanofluids can be divided into three broad categories. The first category, Category I, includes all nanofluids that were purchased from manufacturers already dispersed in a base fluid, including a sometimes proprietary surfactant. These nanofluids were purchased at the highest concentration possible in order to allow for several subsequent dilutions once received. Category II includes all nanofluids that are composed of commercially-bought nanoparticle powders which were then dispersed in chosen base fluids at MIT. By starting with just the nanoparticle powder, there was the freedom to create several types of nanofluids. The third category of nanofluids, Category III, are those that were synthesized from scratch at MIT and include gold dispersed in water, which was created using a citrate reduction process [22], as well as emulsions of water droplets in poly-\( \alpha \)-olefin (PAO) oil, a polymeric synthetic motor oil, titled SpectraSyn 2C, purchased from Exxon Mobil Corporation, Houston, TX [81]. For the gold nanoparticles described in this group, the type of base fluid and surfactant was limited by the known synthesizing technique. For the water-in-PAO emulsions, several water concentrations were studied.
In order to examine the rheological and thermal properties as a function of volume fraction, several preparations at a variety of concentrations were needed. For Category I fluids the high-concentration as-received nanofluid was diluted by first sonicating the original container in an ultrasonic bath (Branson Bransonic 2210R-MTH, Danbury, CT) capable of generating ultrasonic pulses of 90W at 47 kHz, for about two hours in order to ensure that the nanoparticles were evenly dispersed throughout the container, and not settled at the bottom. A second sonication technique employed to further break-up agglomerations and disperse particles uniformly, consisted of an ultrasonic probe (Sonics & Materials, Inc. VCX 750, Newtown, CT) capable of producing a power output of 750W at 20 kHz. The ultrasonication process was conducted by inserting the tip of the probe ~5 cm into the fluid and then operating it on pulsed mode, whereby the probe is turned on for two seconds, followed by one second of rest time to allow for the agglomerations to resettle underneath the probe tip. The ultrasonication was continued until the amount of energy transmitted to the sample by the probe had reached 15,000 J.

After the sonication was completed, a pipette was used to withdraw the proper\(^1\) amount of nanofluid, and subsequently place it in a new container. A different pipette was used to measure-out the appropriate amount of the base fluid used for the dilution. This base fluid was then added to the previously withdrawn nanofluid. The new diluted mixture was then sonicated to ensure complete mixing. The process was repeated for each nanofluid concentration.

For Category II fluids, for each dilution the proper amount of nanoparticle powder was weighed and then added to a new container. The chosen base fluid was then added to this container, and the mixture was sonicated in order to ensure uniform dispersion of the nanoparticles.

---

\(^1\) The terms "proper" and "appropriate" used in this section refer to the calculated amount of nanofluid, nanoparticle powder, surfactant, or base fluid necessary to achieve the desired diluted volume fraction.
nanoparticles. If a surfactant was used, then the process included first placing the chosen base fluid in a new container, adding the appropriate amount of surfactant to the base fluid, and then sonicating in the ultrasonic bath for an hour to allow for full dispersion of the surfactant. The measured amount of nanoparticle powder was then added to the base fluid/surfactant mixture, and the entire composite was then sonicated.

For Category III fluids, depending on the type of nanofluid, different dilution methods were used. For the gold-in-water nanofluid synthesized at MIT, the concentrated batch was made by using the aforementioned citrate reduction process. In order to create several dilutions of this nanofluid, the same process utilized for Category I fluids was employed. For the water-in-PAO emulsions, a similar process to that used for Category II fluids containing surfactant was applied, whereby the proper amount of PAO oil was added to a new container, followed by the addition of the appropriate amount of surfactant. This mixture was then sonicated in order to ensure thorough mixing. Finally, the proper amount of water was gradually added to the PAO oil/surfactant mixture while it was being sonicated by the ultrasonic probe, until 15,000 J of energy had been transmitted to the sample.

3.2 Steady-flow Rheology

Rheological measurements were conducted using two instruments: a stress controlled AR1000-N rheometer and a stress-controlled AR-G2 rheometer (both TA Instruments, New Castle, DE). A cone-and-plate geometry was employed, for which the cone had a diameter of 60 mm, a cone angle, β, of 1°, and a truncation gap of 28 μm. Because it is impossible to manufacture a cone with a geometrically perfect tip, the tip is
instead cut off at a pre-determined height, also known as the truncation gap. This gap is the distance above the Peltier plate that the cone operates at during rheological testing.

For the AR1000-N rheometer, the specifications state that the minimum and maximum torque, \( \Gamma \), achievable are 0.1 \( \mu \text{N}\cdot\text{m} \) and \( 1 \times 10^6 \mu \text{N}\cdot\text{m} \), respectively, while the minimum and maximum angular velocity, \( \dot{\phi} \), are \( 1 \times 10^{8} \text{ rad/sec} \) and 100 rad/sec, respectively. On the other hand, the AR-G2 has the ability to apply torques ranging from 0.01 \( \mu \text{N}\cdot\text{m} \) to \( 2 \times 10^9 \mu \text{N}\cdot\text{m} \), and can achieve rotational speeds from \( 1.4 \times 10^{-9} \text{ rad/sec} \) up to 300 rad/sec.

The applied shear rate, \( \dot{\gamma} \), is related to the angular velocity of the rheometer through a proportionality constant that is dependent on the cone angle of the geometry being used. This relationship for a cone-and-plate geometry is given as,

\[
\dot{\gamma} = \frac{1}{\tan \beta} \dot{\phi} .
\]  

(3.1)

The shear stress, \( \tau \), is related to the torque applied by the rheometer through a proportionality constant that is dependent on the radius, \( R \), of the cone-and-plate geometry being used, and is given as,

\[
\tau = \frac{3}{2\pi R^3} \Gamma .
\]  

(3.2)

The steady shear viscosity was measured by imposing a constant shear rate (or shear stress) on the sample and allowing for \( \tau \) (or \( \dot{\gamma} \)) to obtain a steady state value. Once the steady state value was reached, the viscosity \( \eta \) was subsequently calculated via the definition \( \eta = \tau/\dot{\gamma} \). The sample was then subjected to a new shear rate (or shear stress) and the process was repeated. Several viscosity data points at various shear rates (or shear stresses)
Figure 3-1: Viscosity versus shear rate results for the N1.0 calibration fluid when tested on both the AR1000-N and AR-G2 rheometers using the 6 cm 1° cone.

were recorded in order to accurately investigate the non-Newtonian properties of the sample.

It was determined that the aforementioned cone allowed for the widest range of shear rates with the most accuracy, when compared with other available geometries. Using a low-viscosity calibration fluid (N1.0 from Cannon Instrument Company, State College, PA) it was calculated that the average viscosity was accurate to within ±2.0% when tested over a shear rate range from 2 s⁻¹ to 2000 s⁻¹. Figure 3-1 plots the results of this test for both the AR1000-N and the AR-G2 rheometers. All samples discussed were tested at room temperature (25°C) unless otherwise noted.

In order to verify the accuracy of the predictions made by the Einstein-Batchelor correlation a fluid containing monodisperse silicon dioxide (Fuso Chemicals, Osaka, Japan) particles with an average diameter of 300 nm was created by dispersing the particles in ethylene glycol at various volume fractions. The results of the rheological testing are shown in Figure 3-2. Figure 3-2(a) plots viscosity versus shear rate and indicates that the fluids at each concentration exhibit a slight amount of shear thinning behavior. Figure 3-2(b) plots
average viscosity versus volume fraction. The results compare well with the Einstein-Batchelor correlation.

Creep tests were conducted by imposing a constant step input of shear stress, \( \tau_0 \), on the sample. This stress was held constant for the entirety of the test, during which time the shear response, \( \gamma(t) \), was measured. From it the creep compliance, \( J(t) \), was calculated by the definition \( J(t) = \gamma(t)/\tau_0 \). Because the pre-yield-stress viscosity is difficult to accurately measure using steady-state flow tests, creep tests were employed. By conducting creep tests at several imposed shear stresses lower than the yield stress, the viscosity at each of these points can be calculated by taking the inverse of the slope of the compliance versus time curve for each imposed shear stress.

### 3.3 Dynamic Light Scattering

Dynamic light scattering (DLS) is a non-invasive method for measuring the average size and distribution of a population of particles dispersed in a liquid medium. A Malvern Zetasizer Nano (Malvern Instruments, Southborough, MA) was used to conduct average
particle size measurements for particle sizes ranging from 0.6 nm to 6 μm at temperatures ranging from 2°C to 90°C using a 4.0 mW, 633 nm red laser.

As was discussed earlier, small particles dispersed in liquids undergo Brownian motion. Due to this constant motion, the light scattered by the particles will continually change with time. In order to gather information about the particles, these fluctuations in scattered light intensity are recorded, and subsequently, the convoluted data is plotted on a correlation curve. Figure 3-3 plots two typical correlation curves as a function of time. The correlation coefficients are given by,

$$ G(\tau) = \int_{-\infty}^{\infty} I(t)I(t+\tau)dt, $$

where $\tau$ is the delay time, $I$ is the intensity of scattered light, and the correlation coefficient is normalized, such that $G(\infty)=1$. For the smaller and therefore faster diffusing ovalbumin particles, the measured correlation has decayed to the baseline value after less than 100 μs, while the larger silicon dioxide particles require nearly 1000 μs to reach the baseline value [82].
In order to obtain information regarding the size of the dispersed particles, the diffusion coefficient is calculated by fitting an exponential to the correlation curve. This exponential is given by,

\[ \int I(t)I(t+\tau)dt = B + A e^{-2q^2Dr}, \]  

where \( B \) is the baseline, \( A \) is the amplitude, and \( D \) is the diffusion coefficient. The scattering vector, \( q \), is given by

\[ q = \frac{4\pi \hat{n}}{\lambda_v} \sin\left(\frac{\theta}{2}\right), \]

where \( \hat{n} \) is the solvent refractive index, \( \lambda_v \) is the vacuum wavelength of the laser, and \( \theta \) is the scattering angle.

Once the diffusion coefficient has been calculated, the hydrodynamic particle radius, defined as the radius of a hard sphere that diffuses with the same speed as the particle under examination, can be computed from the Stokes-Einstein equation, given as,

\[ R_H = \frac{kT}{6\pi\eta D}, \]

where \( R_H \) is the hydrodynamic radius, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( \eta \) is the viscosity of the base fluid. It should be noted that this hydrodynamic radius is an average value, weighted by the particle scattering intensity.

Along with the average particle size, the DLS system has the ability to measure how polydisperse a population of particles is. The polydispersity index (PDI) is calculated from the coefficients of the correlation function, or, if assuming a Gaussian size distribution, by,

\[ \text{PDI} = \frac{\sigma^2}{(2R_H)^2}, \]
where $\sigma$ is the standard deviation. Furthermore, the PDI has a value between zero and one, and for a sample to be considered monodisperse, the PDI must be less than 0.1.

In order to ensure accuracy of the DLS system, a calibration standard was utilized. The same fluid composed of monodisperse 300 nm SiO$_2$ particles in EG that was used to verify the accuracy of the Einstein-Batchelor correlation was again employed. Since the DLS system measured an average diameter of 292.5 nm, which is within 3% of the stated size, its accuracy is confirmed. Furthermore, the particles were measured to have a PDI of 0.058 which indicates that they are indeed monodisperse.

One important limitation of performing DLS measurements on fluids containing nanostructured dispersions is that the solutions must be dilute enough so that the impinging laser light can penetrate through at least part of the test cell. If the solution is too concentrated, multiple scattering and particle interaction can affect the results. Since the minimum and maximum sample concentrations that can be measured depend on the size, optical properties, and the polydispersity of the dispersed particles, these limits must be determined experimentally for each suspension. Therefore, in order to perform DLS measurements, the samples were first diluted until they appeared translucent.

### 3.4 Zeta Potential

The zeta potential is a repeatable estimate of the surface charge of a particle suspended in another medium. As shown in Figure 3-4, a negatively charged particle will attract positively charged ions, and the density of these ions can be categorized into three regions. The first region consists of densely packed ions which are strongly bound to the particle and tend to translate with it. The second region extends from the edge of the first
region to the slipping plane, or Stern plane. This region, known as the Stern layer, consists of loosely attached ions. The third region is mainly comprised of the bulk fluid, and is known as the Gouy-Chapman layer. In this region the charge on the particle decreases exponentially to that of the bulk fluid. Therefore, the zeta potential is taken as the difference between the charge at the Stern plane and the charge of the bulk fluid [84].

The zeta potential of a solution is measured using the same DLS system discussed in the previous section. However, for zeta potential measurements, a voltage is applied across a pair of electrodes in the test cell containing the particulate suspension. The charged particles therefore accelerate towards the oppositely charged electrode. This motion is opposed by the viscosity of the base fluid and once equilibrium is reached, the particles reach a constant velocity. The particle velocity is determined using laser Doppler electrophoresis, which consists of measuring the frequency shift of scattered light that is caused by the particle motion [83]. Figure 3-5 illustrates this measurement technique by comparing the frequency of scattered light for a particle with no velocity, to one with a finite velocity.

After measuring the frequency shift, the particle velocity can be calculated from,
Figure 3-5: Schematic showing that the frequency of scattered light ($F_1$) will be the same as the incident laser ($F_i$) for stationary particles, but will be of a different frequency ($F_2$) if the particles are moving, as reported by [83].

$$\Delta f = 2U \sin(\theta/2)/\lambda,$$

(3.8)

where $\Delta f$ is the frequency shift, $U$ is the particle velocity, $\theta$ is the scattering angle, and $\lambda$ is the laser wavelength. Once the particle velocity has been calculated, the zeta potential can be determined from the Henry equation given as,

$$U_z = \frac{2\varepsilon_c z f(\kappa a)}{3\eta},$$

(3.9)

where $\varepsilon_c$ is the dielectric constant, $z$ is the zeta potential, $\eta$ is the viscosity of the base fluid, and $f(\kappa a)$ is the Henry function. The Henry function is dependent on both $\kappa$ and $a$, where $1/\kappa$ is known as the Debye length, the length over which ions in solution will screen out an electric field, and $a$ is the radius of the particle. Therefore, the product $\kappa a$ is the ratio of a particle's radius to the Debye length. It should be noted that zeta potential measurements could only be conducted on water-based fluids because of the low ionic strength of non-aqueous fluids.
3.5 Transmission Electron Microscopy

The transmission electron microscope (TEM) functions in a very similar manner to a typical light microscope, but uses electrons instead of light to examine samples. Because of this difference, TEM's have a substantial advantage over light microscopes in being able to examine smaller specimens. Since the wavelength of light is 600 nm, structures smaller in size than this can not be examined by a light microscope. However, TEM's can have resolutions a thousand times better than light microscopes and can distinctly see structures on the order of a few angstroms.

A TEM works by emitting electrons from a source at the top of the microscope. The electrons then travel through the vacuum in the microscope column and are subsequently focused by a series of electromagnetic lenses into a fine beam. This electron beam travels through the specimen being studied, which acts to scatter some of the electrons. The remaining unscattered electrons impinge on a fluorescent screen and give rise to a “shadow image” of the specimen, with the different structures having varied darkness depending on their inherent densities. The images shown in this work were captured by a CCD camera.

The TEM was a JEOL 2011 (JEOL Ltd., Tokyo, Japan), which operates at 200 kV, and has a resolution of 0.19 nm. The specimens were placed on 200 mesh carbon film grids purchased from Electron Microscopy Sciences, Hatfield, PA. Preparation of each sample included placing a drop of a diluted nanofluid onto a new grid and allowing for it to dry overnight.

One important limitation of performing TEM measurements on nanoparticles is that when the solution is placed on the grid and allowed to dry, aggregation of the nanoparticles can occur. This phenomenon can indicate a degree of clustering that may be greater than
what is present in the bulk sample. Therefore, characterization using this method must be
performed with caution. In general, TEM imaging for this application is only useful for
gaining information about primary particle sizes, and not about cluster sizes or degree of
aggregation. When TEM is used in conjunction with DLS, the combination can prove to be
very useful for gaining accurate information about particle size, shape, and degree of
aggregation.

3.6 Transient Hot-Wire Method

In order to measure the thermal conductivity of fluids, a transient hot-wire method
was adopted. This method was employed in the majority of the reports discussed in the
previous chapter [41], [35], [36], [33], and is known to be highly accurate. Furthermore, the
method is quick and almost completely eliminates the effects of natural convection [11].
The in-house apparatus consists of a 15 cm-long platinum wire that is immersed horizontally
in the fluid being tested. The wire has a diameter of 25 μm and acts as both the heating
element and the thermometer. The platinum wire is insulated with a 1.5 μm layer of Isonel
in order to avoid problems related to measuring electrically conducting fluids [85]. The test
cell is long enough so as to negate wire end effects, and therefore requires a sample volume
of at least 40 ml.

The reason for the term “transient” in the name of this technique, is that the
electrical power is supplied to the wire in an abrupt and brief fashion. Joule heating occurs,
and subsequently, the temperature of the wire increases. This rise in temperature as a
function of time is dependent on the heat transfer properties of the fluid being tested, and
from this response, the thermal conductivity of the fluid can be calculated from a derivation of Fourier’s Law,

\[ k = \frac{q}{4\pi(T_2 - T_1)} \ln \left( \frac{t_2}{t_1} \right), \]  

(3.10)

where \( q \) is the applied electric power and \( T_1 \) and \( T_2 \) are the temperatures at times \( t_1 \) and \( t_2 \). Therefore, based on the wire’s resistance as a function of temperature, the thermal conductivity of the sample can quickly be calculated [41].

The thesis written by Ma [86] describes this method in greater detail, including calibrations performed as well as possible thermophoretic and electrohporetic effects.
Chapter 4

Results and Discussion: Commercial Nanofluids

This chapter details those nanofluids that were purchased as such directly from manufacturers (Category I nanofluids). These nanofluids differ from those described in the next chapter which were either completely synthesized from scratch at MIT (Category III nanofluids), or for which a nanoparticle powder was purchased from a commercial retailer and then subsequently dispersed in a chosen base fluid at MIT (Category II nanofluids). This chapter includes a description of each material obtained from the manufacturers, followed by the results of nanoparticle characterization using TEM imaging, DLS, and zeta potential measurement techniques, and finally the results from rheological and thermal conductivity testing.

4.1 \( \text{Al}_2\text{O}_3 \)-based Nanofluids

Three separate \( \text{Al}_2\text{O}_3 \)-based nanofluids were obtained from two different manufacturers. These include: 1) \( \text{Al}_2\text{O}_3 \) in water with a proprietary surfactant at an as received volume fraction of 21.4 vol.% and with a stated particle size of 47 nm from Nanophase Technologies Corporation, Romeoville, IL, 2) \( \text{Al}_2\text{O}_3 \) in water without a surfactant at an as received volume fraction of 7.94 vol.% and with a stated particle size of
47 nm, also from Nanophase Technologies Corporation, and 3) Al₂O₃ in EG with sodium dodecylbenzenesulfonate (NaDBS) as the surfactant at an as-received volume fraction of 5 vol.% and with a stated particle size of 35 nm from Meliorum Technologies, Inc., Rochester, NY.

The three Al₂O₃-based fluids were first diluted to the following concentrations using the procedure detailed in Chapter 3: the Al₂O₃-water-surfactant fluid was diluted to 15, 10, 5, 3, 2, and 1 vol.%; the Al₂O₃-water fluid was diluted to concentrations of 5, 3, and 1 vol.%; and the Al₂O₃-EG fluid was diluted to concentrations of 4, 3, 2, and 1 vol.%.

4.1.1 Nanoparticle Characterization

DLS measurements and TEM imaging were conducted on all three fluids, while zeta potential measurements were only performed on the two water-based fluids. The results of the DLS and zeta potential testing are shown in Table 4-1. As can be seen from the table, in all three cases the DLS-measured particle size is much larger than that reported by the manufacturers. For the water-based fluids, the average particle size was measured to be 149 nm, which is 3.17 times larger than the stated value of 47 nm. This factor of 3.17 is important and will be returned to in the next section. The EG-based fluid had an average
particle size of 186 nm, which is more than five times greater than the stated size. Furthermore, as is evident from the results, all three fluids can be considered polydisperser because the PDI’s are all greater than 0.1. Lastly, the zeta potential measurements on the two water-based fluids indicate that the addition of a surfactant acts to lower the charge of the suspended particles.

Figure 4-1 shows the TEM images for the Al₂O₃-water and Al₂O₃-EG fluids from which we can see that for the Al₂O₃-water fluid the particles have a wide range of sizes, confirming the results from the DLS measurement. However, the primary particle sizes appear to be much smaller than the reported DLS diameter, and in fact, do not exceed 100 nm. Therefore, the conclusion can be drawn that the particles agglomerate to form clusters, something that DLS, but not TEM, allows examination of. The TEM of the Al₂O₃-EG fluid also displays a similar trend. The “spotty” background may be due to the residue left by the ethylene glycol, which appears less “clean” after evaporation.
4.1.2 Rheological Measurements

The AR1000-N rheometer was used to conduct measurements on the Al₃O₃-based fluids. Figure 4-2 plots the results of viscosity versus shear rate for the Al₃O₃-water-surfactant and Al₃O₃-water fluids, respectively. From Figure 4-2 it can be seen that for both materials the low concentrations appear to be Newtonian, while at higher concentrations, slight shear thinning is observed. This result is very similar to that reported by Pak and Cho [38] for Al₂O₃ nanoparticles dispersed in water shown in Figure 2-20(a). Furthermore, the viscosities of both the Al₂O₃-water-surfactant and Al₂O₃-water fluids increase with increasing concentration, as expected.

Figure 4-3 plots the results of viscosity versus shear rate testing for the Al₂O₃-EG fluid. As can be seen from the plot, a slight amount of shear thinning is observed at all concentrations. However, more noteworthy is the fact that as the particle concentration is increased the viscosity decreases, opposite to what is expected or what was observed for the Al₂O₃-water materials. As will be discussed in detail later, these results may be due to the presence of water in the as-received high-concentration sample. The reason for this
Figure 4-3: Viscosity versus shear rate for the $\text{Al}_2\text{O}_3$-EG fluids at various nanoparticle loadings.

Figure 4-4: Average viscosity versus volume fraction for the three $\text{Al}_2\text{O}_3$ fluids including the calibration results for the $\text{SiO}_2$-EG fluid and the Einstein-Batchelor correlations for water and EG as base fluids.

Hypothesis is that when exposed to the atmosphere, ethylene glycol readily absorbs moisture present in the air. Furthermore, at 25°C ethylene glycol has a viscosity that is approximately 16 times greater than that of water. Therefore, if it is indeed the case that water is present in the original high-concentration sample, as it is diluted to produce lower volume fraction fluids, the percentage of water present will subsequently be reduced, leading to an increase in viscosity.

Figure 4-4 plots a summary of average viscosity versus volume fraction for the three $\text{Al}_2\text{O}_3$ fluids including the calibration results for the $\text{SiO}_2$-EG fluid and the Einstein-
Batchelor correlations for water and EG as base fluids. Besides the fact that for the Al₂O₃-EG fluid the viscosity decreases with increasing concentration, the other unusual result is that for the Al₂O₃-water-surfactant and Al₂O₃-water samples the viscosities measured do not follow the Einstein-Batchelor correlation, but instead exhibit a significantly more rapid increase in viscosity as concentration is increased. This trend is similar to that reported by Pak and Cho [38] and shown in Figure 2-20(b). However, Pak and Cho measured a viscosity almost 300 times greater than that predicted by the Einstein-Batchelor correlation at a shear rate of 19.2 s⁻¹, whereas at the same concentration (10 vol.% ) and shear rate the fluids discussed here only exhibited a viscosity of about twice that predicted by the Einstein-Batchelor correlation. Furthermore, Pak and Cho hypothesized that these anomalous results may be due to the irregular and rough shape of the dispersed particles, or to viscoelastic effects [38].

For the materials described here, one explanation for the behavior observed is to assume that the particles dispersed in water are not actually separate, but are instead agglomerating to form clusters, as was confirmed by the DLS measurements. An example of this type of agglomeration is shown in Figure 4-5, where scanning electron microscope (SEM) images of fused SiO₂ are shown as an example of the degree to which particles can cluster during production. These clusters therefore contribute to there being a larger effective volume fraction of solids for a given mass fraction [87]. Essentially, because the clusters form random chain-like structures, they have a larger excluded volume fraction than if the particles were separated into their primary constituents.

Equations 4.1 and 4.2 further explain this phenomenon by defining how the nominal volume fraction is calculated for a given mass of particles, and how therefore, there is a
Figure 4-5: Scanning electron microscope (SEM) image of fumed SiO₂ aggregates which are formed by the fusion of the 14 nm primary particles to form a chain-like structure, as reported by [87].

The multiplying factor that is used to arrive at the effective volume fraction of particles. The nominal volume fraction is given as,

\[ \phi_{\text{nominal}} = \frac{m_{\text{Al₂O₃}} / \rho_{\text{Al₂O₃}}}{m_{\text{Al₂O₃}} / \rho_{\text{Al₂O₃}} + m_{\text{H₂O}} / \rho_{\text{H₂O}}} \],

(4.1)

where \( m \) is the mass of the nanoparticles or water, and \( \rho \) is the density of the nanoparticles or water. The effective volume fraction can then be found from,

\[ \phi_e = \text{M.F.} \cdot \phi_{\text{nominal}} \],

(4.2)

where M.F. is the multiplying factor. For the Al₂O₃-water-surfactant and Al₂O₃-water fluids, by multiplying the nominal volume fraction values by a multiplying factor of 3.14, the points that had originally lied above the Einstein-Batchelor correlation could now be accurately predicted by the correlation. This multiplying factor of 3.14 is almost identical to the value of 3.17 measured in the previous section via DLS. Therefore, it can be concluded that the
Al₂O₃ particles dispersed in water have agglomerated to such a degree that they appear to be roughly three times larger than they actually are.

4.1.3 Thermal Conductivity Measurements

Figure 4-6 plots thermal conductivity enhancement percentage versus nanoparticle volume fraction, where the thermal conductivity enhancement is given as

\[ k_{\text{enhancement}} \% = \left( \frac{k_c(\phi)}{k_f} - 1 \right) \times 100, \]  

(4.3)

where, as before, \( k_c \) and \( k_f \) are the effective thermal conductivity of the composite and the thermal conductivity of the base fluid, respectively. The plot includes the Maxwell effective medium theory predictions for water and ethylene glycol when interfacial resistance is not present (Eq. 2.1) and when it is present (Eq. 2.6). As can be seen from the plot, the Maxwell theories (with and without interfacial resistance) predict higher enhancements than is observed for the Al₂O₃-water-surfactant fluid. Furthermore, the maximum enhancement achieved for this fluid was 26.4% at a concentration of 21.4 vol.%. For the Al₂O₃-water fluid, on the other hand, the Maxwell theory including interfacial resistance accurately
Figure 4-7: Thermal conductivity enhancement percentage versus viscosity enhancement percentage for the three Al₂O₃ fluids at concentrations up to 5 vol.%. Predicts the enhancement for volume fractions up to 5 vol.%. The Al₂O₃-EG fluid appears to have the greatest enhancement versus volume fraction slope, and correlates well with the Maxwell theory for EG when no interfacial resistance is included.

Figure 4-7 plots thermal conductivity enhancement percentage versus viscosity enhancement percentage, where the viscosity enhancement is given by

\[ \eta_{\text{enhance}} \% = \left[ \frac{\eta_c(\phi)}{\eta_f} - 1 \right] \times 100, \]  

where \( \eta_c \) and \( \eta_f \) are the effective viscosity of the composite and the viscosity of the base fluid, respectively. As can be seen from the plot, in terms of the two water-based fluids, the viscosity does not differ much between the two, even though a surfactant is present in one of them. Furthermore, because the Al₂O₃-water-surfactant fluid has lower thermal conductivity enhancement at each concentration, it is less desirable than its non-surfactant counterpart. The Al₂O₃-EG fluid, on the other hand, exhibits a very advantageous behavior, as its thermal conductivity enhancement increases with increased particle loading while the viscosity enhancement continues to decrease, and is in fact negative for all particle concentrations. As was speculated in section 4.1.2, this trend may be due to the presence of...
a small amount of water in the as-received high concentration fluid. Ma [86] showed that by exposing ethylene glycol to the atmosphere for a period of 33 days, the thermal conductivity can be enhanced by 4.0% by the absorption of water. This hypothesis will be studied in more detail in the next section which discusses the results found for gold nanoparticle fluids purchased from the same company.

4.2 Au-based Nanofluids

Two different Au-based nanofluids were obtained from Meliorum Technologies, Inc. These include: 1) Au in water without a surfactant at an as received concentration of 0.27 vol.% and with a stated particle size of 15 nm, and 2) Au in ethylene glycol without a surfactant at an as received concentration of 0.3 vol.% and with a stated particle size of 15 nm. The two Au-based fluids were first diluted to concentrations of 0.2, 0.1, 0.05, and 0.01 vol.%.

4.2.1 Nanoparticle Characterization

To begin the characterization process, DLS and TEM measurements were conducted on both fluids. However, for the Au-water fluid no particles were found using either of the aforementioned methods. Viscosity measurements, which will be discussed in detail in the next section, further indicated that there were in fact no particles dispersed in the fluid. For the Au-EG fluid, DLS-measured diameter was 176 nm with a PDI of 0.205. This is much larger than the manufacturer's stated size of 15 nm, and because the PDI is greater than 0.1, the particles can be considered polydisperse.
The TEM image for this particular fluid is shown in Figure 4-8, from which it can be noted that the primary particles appear to be much smaller than the 50 nm scale bar. Dustyn Sawall of Ford Motor Company performed the TEM imaging on this sample and measured the size of the primary particles to be in the range of 3-5 nm, which is smaller than the manufacturer’s stated particle size. Furthermore, the particles appear to be more irregularly shaped than the Al₂O₃-based fluids. Ultimately, as with the Al₂O₃-based fluids, since the DLS measurements indicate a particle size which is much larger than that seen via TEM imaging, it can be concluded that the particles agglomerate to form much larger clusters.

4.2.2 Rheological Measurements

The AR1000-N rheometer was used to conduct measurements on the Au-based fluids. Figure 4-9(a) plots the results of viscosity versus shear rate for the water-based fluid, from which it can be seen that all five of the dilutions exhibit Newtonian behavior and
overlap each other. From Figure 4-9(b) it can be seen that the average viscosity does not increase with increasing volume fraction as is expected and shown via the Einstein-Batchelor correlation. Instead, the average viscosity remains constant and is equal to that of the base fluid.

Figure 4-10(a) plots the results of viscosity versus shear rate for the EG-based fluid, from which it can be seen that all five dilutions exhibit slight shear thinning behavior. Furthermore, from Figure 4-10(b) it is seen that, as with the Al₂O₃-EG fluid from Meliorum Technologies, as the particle concentration is increased the viscosity decreases, opposite to what is predicted by the Einstein-Batchelor correlation. It is again hypothesized that this behavior is due to the presence of water in the as-received high concentration fluid. In order to test this theory a boil-off test was employed. This involved first measuring the mass of the sample, followed by heating the sample in an oven at atmospheric pressure and a temperature of 110°C for 10 minutes. This temperature was chosen because it is higher than the boiling point of water, but lower than that of EG. Once the evaporation phase was completed, the sample was again weighed and its viscosity was tested at 25°C. From the changes in mass it was calculated that there existed approximately 15% water in the original
0.3 vol.% sample. Furthermore, as is shown in Figure 4-10(b), for the high-concentration sample, the viscosity increased by approximately 20%.

In order to further confirm the hypothesis that water was present in the as-received sample, ATR-FTIR analysis was performed by Jack Ma, and is described in detail in [86]. Figure 4-11(a) plots the ATR absorption spectra for the Au-EG fluid along with water and EG. As can be seen from the plot, there is a peak for water at about 1650 cm⁻¹. For Au-EG at this wavenumber there is a small bump, while for EG there is no absorption at this wavenumber, indicating that there is the presence of a small amount of water in the Au-EG sample. To estimate just how much water is present three separate fluids containing different concentrations of water in EG were prepared. The three volume fractions of water are 3.3, 6.7, and 10 vol.%.

Figure 4-11(b) plots the ATR absorption spectra for these three samples along with the Au-EG sample. From the plot it can be seen that the height and area of the peak for the mixture containing 6.7 vol.% water in EG is similar to that for the Au-EG fluid, indicating that approximately this amount of water was present in the original 0.3 vol.% Au-EG fluid.
4.2.3 Thermal Conductivity Measurements

The thermal conductivity of the Au-water sample was tested at the as-received concentration of 0.27 vol.%. The thermal conductivity enhancement was calculated to be about -0.2%, which can be approximated as having an enhancement of zero with an error
within that of the testing apparatus. This result further confirms the hypothesis of no gold nanoparticles being present in the Au-water fluid, and therefore precludes measurements from being completed on the dilute samples.

The results of thermal conductivity measurements for the three most concentrated samples of the Au-EG fluid are plotted in Figure 4-12. From Figure 4-12(a), which plots thermal conductivity enhancement percentage versus volume fraction, it can be seen that the enhancements measured far exceed those predicted by the Maxwell effective medium theory, both with and without the inclusion of interfacial resistance. Figure 4-12(b) plots thermal conductivity enhancement versus viscosity enhancement, from which it can be seen that as the thermal conductivity enhancement increases with increased particle concentration, the viscosity enhancement decreases, and becomes more negative. This is the same trend that was observed for the aforementioned Al₂O₃-EG fluid, and as was shown via ATR-FTIR testing, is due to the presence of water.
4.3 Ag-based Nanofluids

A suspension of Ag nanoparticles dispersed in ethylene glycol was purchased from Sigma-Aldrich, St. Louis, MO at an as-received concentration of 10 wt.%. Since only approximately 25 ml was ordered, and the THW apparatus requires about double that to conduct measurements, the fluid was diluted by half to 5 wt.%. Whether or not a surfactant is present is unclear. The Ag nanoparticles were stated by the manufacturer to be 50 nm in diameter.

4.3.1 Nanoparticle Characterization

DLS and TEM measurements were conducted on the Ag-EG fluid, while zeta potential measurements could not be performed because of the presence of a non-aqueous base fluid. The DLS measurements indicated the particle size as 58.13 nm with a PDI of 0.262. Therefore, while the average particle size measured is very close to the stated size, the particles are polydisperse. However, this fluid at first appears promising because it is the first for which the measured particle size is within ±10 nm of the stated size.

Figure 4-13 shows the TEM image of the Ag-EG fluid, from which we can see that the particles are generally spherical and indeed have a variety of diameters. Furthermore, it is obvious that the primary particle size is on average about half the size of the 100 nm scale bar. Therefore, the conclusion can be drawn that because the primary particle size seen via TEM correlates well with the average particle size measured using DLS, minimal agglomeration is present in this fluid.
4.3.2 Rheological Measurements

The AR-G2 rheometer was used to conduct measurements on the Ag-EG fluid. Figure 4-14 plots the results as viscosity versus shear rate. From the plot we can see that the fluid behaves in a Newtonian manner that mirrors that of the base fluid, EG. The average viscosity was calculated to be 0.0222 Pa·s, which is 36% greater than the viscosity of EG.

4.3.3 Thermal Conductivity Measurements

The thermal conductivity of the Ag-EG fluid was tested and found to have a value of 0.253 W/m·K, which is the same as that of the base fluid. Therefore, no enhancement was achieved by dispersing the Ag particles in EG. Because of the small size of the particles suspended, and the well-dispersed nature of the particles, this is a rather disappointing result,
pointing to the fact that other variables, besides nanoparticle material, nanoparticle size, and degree of particle aggregation, are at play.

4.4 MWCNT-based Nanofluids

Multi-walled carbon nanotubes (MWCNTs) were purchased from Zyvex Corporation, Richardson, TX, dispersed in water using a proprietary surfactant at an as-received nanotube concentration of 0.2 wt.%. The nanotubes were stated to have an average diameter of 15 nm and an average length of 7.5 μm, with, therefore, an aspect ratio of 500. Prior to testing, the dispersion was diluted to the following concentrations: 0.15, 0.1, 0.05, 0.01, 0.001, and 0.0005 wt.%. 

4.4.1 Nanotube Characterization

TEM imaging was performed on the MWCNT-water sample and the results are shown in Figure 4-15, from which we can see that the MWCNTs are highly networked with
large aspect ratios. Furthermore, the tubes themselves are rather flexible, enabling entanglement and formation of bundles.

4.4.2 Rheological Measurements

The AR1000-N rheometer was used to conduct measurements on the MWCNT-based fluids. Figure 4-16 plots viscosity versus shear rate for all seven dilutions, from which we can see that from Figure 4-16(a), for the two least concentrated fluids (0.0005 and 0.001 wt.%) the behavior is Newtonian and the viscosity is very similar to that of the base fluid, water. The results for the five most concentrated fluids (0.01, 0.05, 0.1, 0.15, and 0.2 wt.%) are plotted in Figure 4-16(b) from which it can be seen that as the shear rate is increased the fluids exhibit what appears to be a shear thinning behavior, until the limiting viscosity is reached, at which point the viscosity does not change with shear rate. Once the highest
shear rate was achieved (2000 s⁻¹), the test was reversed and the shear rate was decreased in increments to a final shear rate of 0.2 s⁻¹. During this second part of the test, for the four most concentrated samples, the viscosity increases dramatically, ultimately reaching a value approximately an order of magnitude greater than the viscosity measured when the test was first begun, and three orders of magnitude greater than the infinite shear viscosity (the viscosity at 2000 s⁻¹). The trends observed in Figure 4-16(b) are very similar to those seen by Ding et al. [51], except that Ding et al. found that their samples exhibited a shear thinning behavior that took place over almost five decades of viscosity for a similar shear rate range.

To further examine these unusual trends, the five most concentrated fluids are plotted in Figure 4-17 as viscosity versus shear stress. From this plot we can see that all fluids, except the 0.05 and 0.2 wt.% samples exhibit a yield stress at the low stress of approximately 0.01 Pa. As the shear rate, and therefore stress, is increased, a constant viscosity similar to that of the base fluid, water, is observed. Once the highest shear stress was achieved (~2.7 Pa), the test was reversed. During this second part of the test it was observed that the viscosity increased rapidly, reaching values four orders of magnitude greater than the infinite shear viscosity.
In order to more clearly understand the trends being observed, and in particular measure the pre-yield-stress viscosity, a creep test was employed by subjecting the 0.2 wt.% sample to eleven different stresses and recording the strain output as a function of time. Figure 4-18(a) plots the results of this test as compliance versus time, from which we can see that for stresses lower than 0.2 Pa, little or no flow is observed, and therefore the yield stress has not been reached. However, at an imposed stress of 0.2 Pa, the sample begins to flow, and this behavior becomes even more apparent as the stress is increased. The viscosity was then calculated for each of the eleven imposed stresses by taking the inverse of the slope of
the compliance versus time curves. These results are plotted in Figure 4-18(b) along with the results of the steady flow test conducted on the 0.2 wt.% sample, as well as the results of a steady flow test when the sample had been pre-sheared. From the plot we can see that the results from the creep test clearly define a yield stress that has a value in the range of 0.05 to 0.5 Pa. The viscosity during the course of the test decreases from a value of approximately 2500 Pa·s to the infinite shear viscosity of approximately 0.0012 Pa·s.

The steady flow test including pre-shearing was conducted by shearing the sample at 2000 s\(^{-1}\) for 60 seconds, immediately followed by a typical steady flow test. From the results we can see that there is a yield stress to begin with, and that the viscosity decreases as the shear stress is increased. Furthermore, when the test was reversed, and the shear rate, or alternatively shear stress, was decreased, the viscosity increased at a slightly quicker rate, but ultimately reached the starting viscosity, essentially forming a loop. The viscosity during this test always remained in the intermediate region between the constant viscosity curve of the first part of the original steady flow test, and the curve defined by the creep test. The unusual behavior exhibited by this fluid can be regarded as shear-induced structuring [88]. Because prior to testing the fluid was sonicated using the ultrasonic bath, the nanotubes may have become highly ordered. Once the testing was performed, and the high shear rate reached, the nanotubes became tangled, leading to higher viscosities and the presence of a yield stress as the shear rate was decreased. The original low viscosity can then only be reached by sonicating the sample again. This behavior can be explained more clearly by taking the example of a box of matches. If the matches are dumped out, it is nearly impossible to put them back into the box without the addition of energy. Only by shaking or vibrating them will they become ordered enough to be placed in the box. Similarly, only
by sonicating will the nanotubes return to a highly-ordered state which allows them to slide easily past one another at low shear rates, leading to low viscosity measurements.

4.4.3 Thermal Conductivity Measurements

The thermal conductivity of the 0.2 wt.% MWCNT-water fluid was tested and found to have a value of 0.592 W/m·K, which is 0.007 W/m·K less than the measured thermal conductivity of water. Therefore, a negative enhancement of -1.2% was achieved by dispersing the MWCNTs in water, which, alternatively, can be approximated as having an enhancement of zero with an error within that of the testing apparatus. For this reason, testing on the more diluted fluids was not performed.
Chapter 5

Results and Discussion: MIT-Synthesized Nanofluids

This chapter details those nanofluids that were either completely synthesized from scratch at MIT (Category III nanofluids), or for which a nanoparticle powder was purchased from a commercial retailer and then subsequently dispersed in a chosen base fluid at MIT (Category II nanofluids). This chapter includes a description of each material obtained from the manufacturers and the dilution procedure, followed by the results of nanoparticle characterization using TEM imaging, DLS, and zeta potential measurement techniques, and finally the results from rheological and thermal conductivity testing.

5.1 Au-based Nanofluids

An Au-water nanofluid was synthesized by employment of a citrate reduction method conducted by Professor Kimberly Hamad-Schifferli at MIT, and in particular, her student Sunho Park. The process was completed by mixing HAuCl₄, sodium citrate, tannic acid, sodium carbonate, and DI water at particular concentrations and in a specific order. The sodium citrate acted as a surfactant, maintaining a well-dispersed atmosphere, and the amount of tannic acid controlled the final particle size. By increasing the amount of tannic acid, the Au particle size can be decreased. For the given recipe the particles were supposed
Figure 5-1: TEM image of the Au-water nanofluid that had been fully synthesized at MIT. TEM imaging performed by Dustyn Sawall (Ford Motor Company).

to have a final average diameter of 11 nm. At the conclusion of the synthesis, the Au nanoparticles were dispersed in water at a concentration of $1.6 \times 10^{-4}$ vol.%.

5.1.1 Nanoparticle Characterization

DLS and zeta potential measurements, as well as TEM imaging were conducted on the Au-water nanofluid. The average particle size measured via DLS was 21 nm, which is only 10 nm greater than expected, making the Au particles the smallest ones dispersed up to this point. The PDI was measured to be 0.252, which indicates that the particles are polydisperse. Furthermore, zeta potential measurements determined that the charge on an individual particle was approximately $-32 \pm 12.45$ mV.

The results of the TEM imaging, which were performed by Dustyn Sawall of the Ford Motor Company, are shown in Figure 5-1, from which we can see that, despite what was measured via DLS, the particles appear to be monodisperse with a diameter that is
approximately 10 nm. The discrepancy between what is seen in the TEM image and what was measured using DLS may be due to the slight agglomeration of particles that can not be seen in TEM images.

5.1.2 Rheological Measurements

The AR1000-N rheometer was used to conduct measurements on the MIT-synthesized Au-water nanofluid. Figure 5-2(a) plots the results as viscosity versus shear rate, from which it can be seen that the fluid appears to be shear thinning. Figure 5-2(b) confirms this and shows that the fluid exhibits appreciable shear thinning up to a stress of approximately 0.02 Pa at which point the viscosity remains relatively constant as the stress is further increased. When the test is reversed, and the shear stress is reduced, hysteresis is observed, indicating that at the start of the test structuring among the nanoparticles was present. This structuring was subsequently broken up once the shear stress reached the critical point of 0.02 Pa. However, when returning to the low stress region on the way down, some structure was reformed, but not to the same degree as at the beginning of the
test. Therefore, the final viscosity is almost three orders of magnitude less than the viscosity at the commencement of the test.

5.1.3 Thermal Conductivity Measurements

The thermal conductivity of the MIT-synthesized Au-water fluid was tested and found to have a value of 0.599 W/m·K, which is the same as that of the base fluid, water. Therefore, no enhancement was achieved by dispersing the Au particles in water. Because of the small size of the particles suspended, this is a rather disappointing result, again pointing to the fact that other variables, besides nanoparticle material, and nanoparticle size, are at play.

5.2 Thermally-Exfoliated Graphite Oxide-based Nanofluids

Thermally-exfoliated graphite oxide (TEGO) was obtained from Professor Robert K. Prud’homme’s research group at Princeton University. TEGO is created by first expanding graphene nanosheets using intercalation of small molecules, followed by rapid heating which acts to exfoliate the graphite sheets to 250 times their original volume. This process produces a material with a maximum reported surface area of 400 m²/g. Because of this enormous surface area, it was hypothesized that TEGO would transport heat in a more efficient manner, improving the thermal properties of the fluid it was dispersed in.

TEGO was dispersed in N-Methyl-2-pyrrolidone (NMP), which is a solvent typically used to dissolve polymers. It has a density of 1.028 g/cm³ and a thermal conductivity of 0.162 W/m·K. NMP was recommended by the group at Princeton as the best solvent for
dispersion of TEGO. The highest concentration achieved without visible settling was 0.25 wt.%. Three dilutions were then made at the concentrations of 0.116, 0.054, and 0.025 wt.%.

5.2.1 TEGO Characterization

TEM imaging was performed on the TEGO-NMP sample and the results are shown in Figure 5-3, from which we can see that the graphene sheets are highly agglomerated to form large structures, on the order of a micron in diameter. Furthermore, it is evident that the individual sheets are very thin, with large surface areas.

5.2.2 Rheological Measurements

The AR1000-N rheometer was used to conduct measurements on the four TEGO-NMP fluids. Figure 5-4 plots the results of the testing as viscosity versus both shear rate and shear stress, from which it can be seen that the three most concentrated samples exhibit
hysteresis. While they demonstrate Newtonian behavior as the shear rate (or shear stress) is increased, when the test is reversed and the shear rate (or shear stress) is decreased, the viscosity increases dramatically, to a value almost three orders of magnitude greater than that of the base fluid. This is very similar to the phenomenon observed for the MWCNT-water fluids discussed in Chapter 4, and may again be due to shear-induced structuring that causes the graphene sheets to become less ordered at higher shear rates, ultimately contributing to an increase in the viscosity of the fluid as the shear rate is reduced. At the concentration of 0.025 wt.% this behavior is not observed, as the fluid remains Newtonian throughout the entirety of the test. For the 0.054 wt.% fluid, slight shear-induced structuring is observed as the viscosity increases by only about one-half of an order of magnitude over the value measured at the commencement of the test.

Figure 5-5 plots infinite shear viscosity as a function of TEGO concentration, from which it can be seen that as the concentration of TEGO is increased the infinite shear viscosity also increases. The most concentrated sample exhibits an infinite shear viscosity 85% greater than that of the base fluid. Comparison with the Einstein-Batchelor correlation
is not possible because the density of the dispersed TEGO is not accurately known, and therefore the wt.% values can not be converted into volume fractions.

5.2.3 Thermal Conductivity Measurements

The thermal conductivity of the 0.25 wt.% TEGO-NMP fluid was tested and found to have a value of 0.168 W/m·K, which is 3.7% greater than the measured thermal conductivity of NMP. Therefore, even though the enhancement is positive, it is still small. Furthermore, it is for the highest loading possible (the addition of more TEGO would have resulted in undesirable settling).

5.3 Fullerene-based Nanofluids

Fullerenes, sometimes called buckyballs, are a family of carbon allotropes, and are composed solely of carbon atoms. Carbon nanotubes fall into this family, however, in this section only spherical forms will be examined. Two different types of fullerenes were
acquired from Nano-C Inc., Westwood, MA: \( \text{C}_{60} \) and \( \text{C}_{60}(\text{OH})_{26} \). \( \text{C}_{60}(\text{OH})_{26} \) is the functionalized form of \( \text{C}_{60} \) and has hydroxyl groups bound to its surface. This allows it to be stably dispersed in water. Fullerenes, on average, have a density of 1.72 g/cm\(^3\) and a thermal conductivity of 0.4 W/m-K. Furthermore, as shown in Figure 5-6, the average diameter of a fullerene is 1.02 nm [89].

Using the \( \text{C}_{60} \) variation, two different nanofluids were created by dispersion in both toluene and PAO oil. The solubility limit of \( \text{C}_{60} \) in toluene is 2.8 mg/ml [90], [91]. Therefore, \( \text{C}_{60} \) was dispersed in toluene at a concentration of 0.3 wt.%. For PAO, the solubility limit was found experimentally to be approximately 0.1 wt.%. The \( \text{C}_{60}(\text{OH})_{26} \) fullerenes were dispersed in water at a concentration of 1.0 wt.%, and visibly appeared to be very stable.

### 5.3.1 Rheological Measurements

The AR-G2 rheometer was used to conduct measurements on the three fullerene-based fluids. Figure 5-7 plots the results for both \( \text{C}_{60} \) in toluene and \( \text{C}_{60} \) in PAO. From both plots we can see that the addition of fullerenes does not act to significantly change the behavior of the fluid. Furthermore, the viscosity is not significantly increased by the
existence of fullerenes. For the C_{60}-toluene fluid the average viscosity is increased by less than 5.0% from 5.36\times10^{-4} Pa·s to 5.62 \times10^{-4} Pa·s, while for the C_{60}-PAO fluid the average viscosity actually decreases by approximately 2%, which is within the error of the rheometer, indicating that the fullerenes do not affect the viscosity. Figure 5-8 plots the rheology results for the C_{60}(OH)_{26}-water fluid, from which it can be seen that, like the two previously discussed fullerene fluids, the addition of the fullerenes does not alter the behavior of the fluid. For this case, the average viscosity actually decreases again, this time by less than 1%, pointing to the fact that the viscosity is not changed by adding fullerenes to water.
Table 5-1: Summary of the results of the thermal conductivity testing on the three fullerene-based nanofluids including the base fluid thermal conductivity as well as the enhancement percentage measured.

<table>
<thead>
<tr>
<th>Nanofluid</th>
<th>Base Fluid Thermal Conductivity (W/m·K)</th>
<th>Nanofluid Thermal Conductivity (W/m·K)</th>
<th>Thermal Conductivity Enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$-toluene</td>
<td>0.143</td>
<td>0.140</td>
<td>-1.9</td>
</tr>
<tr>
<td>$C_{60}$-PAO</td>
<td>0.138</td>
<td>0.138</td>
<td>0</td>
</tr>
<tr>
<td>$C_{60}$(OH)$_{26}$-water</td>
<td>0.612</td>
<td>0.611</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

5.3.2 Thermal Conductivity Measurements

Table 5-1 summarizes the results of the thermal conductivity testing on the three fullerene-based fluids. From the table it can be seen that no enhancement is observed for any of the three fluids, and actually, for the toluene- and water-based fluids a negative enhancement was measured which falls within the error of the testing apparatus. Therefore, negligible enhancement is achieved for any of the three fluids tested.

5.4 Sigma-Aldrich Nanopowder-based Nanofluids

Four different nanoparticle powders (nanopowders) were purchased from Sigma-Aldrich, including SiC, Diamond, Al$_2$CuO$_4$, and Fe$_2$O$_3$. They were subsequently dispersed in water, ethylene glycol, and PAO oil without surfactants following the procedure detailed in Chapter 3, to form twelve different nanofluids. The manufacturer stated size and the concentrations of particles dispersed in the three base fluids are summarized in Table 5-2. It should be noted that while the SiC-PAO fluid is included in this section, it will be discussed in further detail in Section 5.5.
<table>
<thead>
<tr>
<th>Nanoparticle Type</th>
<th>Manufacturer Stated Particle Size (nm)</th>
<th>Concentration in Water</th>
<th>Concentration in EG</th>
<th>Concentration in PAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>45-55</td>
<td>1 vol.%</td>
<td>1 vol.%</td>
<td>1 vol.%</td>
</tr>
<tr>
<td>Diamond</td>
<td>3.2</td>
<td>0.57 vol.%</td>
<td>0.57 vol.%</td>
<td>0.57 vol.%</td>
</tr>
<tr>
<td>Al₂CuO₄</td>
<td>40</td>
<td>10 wt.%</td>
<td>10 wt.%</td>
<td>10 wt.%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>20-25</td>
<td>1 vol.%</td>
<td>1 vol.%</td>
<td>1 vol.%</td>
</tr>
</tbody>
</table>

Table 5-2: Summary of the four nanoparticle powders obtained from Sigma-Aldrich, including the manufacturer stated particle size as well as the concentrations dispersed in water, EG, and PAO oil.

<table>
<thead>
<tr>
<th>Nanofluid</th>
<th>Stated Particle Size (nm)</th>
<th>DLS-Measured Particle Size (nm)</th>
<th>Polydispersity Index (PDI)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-water</td>
<td>45-55</td>
<td>520.1</td>
<td>0.403</td>
<td>-19.8 ± 6.52</td>
</tr>
<tr>
<td>SiC-EG</td>
<td>45-55</td>
<td>296</td>
<td>0.071</td>
<td></td>
</tr>
<tr>
<td>SiC-PAO</td>
<td>45-55</td>
<td>2760</td>
<td>0.516</td>
<td></td>
</tr>
<tr>
<td>Diamond-water</td>
<td>3.2</td>
<td>182.2</td>
<td>0.32</td>
<td>38 ± 4.84</td>
</tr>
<tr>
<td>Diamond-EG</td>
<td>3.2</td>
<td>174.7</td>
<td>0.258</td>
<td></td>
</tr>
<tr>
<td>Diamond-PAO</td>
<td>3.2</td>
<td>9567</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Al₂CuO₄-water</td>
<td>40</td>
<td>170.5</td>
<td>0.166</td>
<td>24.8 ± 7.09</td>
</tr>
<tr>
<td>Al₂CuO₄-EG</td>
<td>40</td>
<td>172.9</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>Al₂CuO₄-PAO</td>
<td>40</td>
<td>672.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-water</td>
<td>20-25</td>
<td>1623</td>
<td>0.487</td>
<td>10.5 ± 3.67</td>
</tr>
<tr>
<td>Fe₂O₃-EG</td>
<td>20-25</td>
<td>740.3</td>
<td>0.182</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-PAO</td>
<td>20-25</td>
<td>1039</td>
<td>0.359</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-3: Results of DLS and zeta potential measurements for the twelve Sigma-Aldrich nanopowder-based nanofluids.

### 5.4.1 Nanoparticle Characterization

Zeta potential measurements and TEM imaging were conducted on the four water-based fluids, while DLS measurements were performed on all twelve nanofluids. Table 5-3 summarizes the results of the DLS and zeta potential measurements, from which it can be seen that none of the twelve samples exhibited particle sizes in the range of those stated by the manufacturer. The smallest particle size recorded was 170.5 nm for the Al₂CuO₄-water
fluid, which is still more than four times greater than the size quoted by the manufacturer. Furthermore, the SiC-EG and Al₂CuO₄-EG fluids were the only two that can be considered monodisperse, both having PDI's less than 0.1. Lastly, the large PDI values for the Diamond-PAO, SiC-PAO, and Al₂CuO₄-PAO fluids are due to the existence of highly-agglomerated particles in the sample.
Figure 5-9 shows the TEM images of the four different types of particles obtained from Sigma-Aldrich. From the TEM image of the SiC particles (Figure 5-9(a)) it can be seen that the primary particle size does vary and therefore the particles can be considered to be polydisperse. Furthermore all of the primary particles appear to be smaller than the 100 nm scale bar, indicating that the DLS measurements observed a large amount of agglomeration among the primary particles. In particular, in the case of the SiC-PAO fluid, if it is indeed accepted that the average primary particle size is 50 nm, then there are approximately 50 particles that cluster together to form one agglomeration.

The diamond nanoparticles (Figure 5-9(b)) also appear to have an average primary particle size that is comparable to the manufacturer stated size of 3.2 nm. Again, large agglomerations, on the order of possibly thousands of particles, could have formed once the particle were dispersed in the base fluid. The same thing could also be true for the Al₂CuO₄ and Fe₂O₃ fluids, because the DLS-measured particle sizes are much larger than the primary particle sizes seen in the TEM images (Figure 5-9(c) and Figure 5-9(d)).

5.4.2 Rheological Measurements

The AR-G2 rheometer was used to conduct measurements on the twelve nanofluids. Figure 5-10 plots the results of the testing performed on the water-based fluids, from which it can be seen that all four fluids exhibit a yield stress, further indicating that the dispersed particles are aggregating to form a network which acts to resist motion, thereby increasing the viscosity. When the highest shear rate (or shear stress) is reached, the viscosity has decreased significantly to a value similar to that of the base fluid. Furthermore, for the diamond nanofluid, hysteresis is observed, demonstrating that the structure that exists at the
commencement of the test is broken down by the shearing forces, and does not rebuild itself as quickly when the shear rate is decreased. This is similar to what was observed for the MWCNT-water fluid discussed in the previous chapter.

Figure 5-11 plots the results of the same testing on the four EG-based fluids, from which it can be seen that the fluids, with the exception of the $\text{Al}_2\text{CuO}_4$-EG fluid, do not demonstrate a yield stress to the same degree as with the water-based fluids. For the $\text{Al}_2\text{CuO}_4$-EG fluid we see that, as with the water-based fluids, there exists a structured network of particles that is broken up as the fluid is sheared. However, for this fluid the
structure does not re-form upon lowering the shear rate, but instead exhibits a Newtonian behavior during the second half of the test while the shear rate is progressively decreased.

Figure 5-12 plots the results of the rheological testing for the four PAO oil-based fluids, from which it can be seen that the fluids exhibit similar behavior to what was observed for the water-based fluids shown in Figure 5-10. For these four fluids, however, once the nanoparticle structures are broken down by the shearing forces, they do not rebuild themselves at the same rate when the shearing is progressively decreased. Instead, we see that the viscosity values at the beginning and end of the complete test (both at low shear rate or low shear stress) are different, indicating that the structure build-up is thixotropic, or equivalently, time-dependent. Furthermore, it should be noted that the increase in viscosity caused by structuring can be approximately three orders of magnitude larger than the infinite shear viscosity.
Table 5-4: Results of the thermal conductivity measurements on the twelve Sigma-Aldrich nanopowder-based nanofluids, including base fluid conductivity, nanofluid conductivity, enhancement percentage, and the enhancement predicted by the Maxwell effective medium theory when no interfacial resistance is included.

<table>
<thead>
<tr>
<th>Nanofluid</th>
<th>Base Fluid Thermal Conductivity (W/m·K)</th>
<th>Nanofluid Thermal Conductivity (W/m·K)</th>
<th>Thermal Conductivity Enhancement (%)</th>
<th>Maxwell Theory Predicted Enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-water</td>
<td>0.606</td>
<td>0.628</td>
<td>3.6</td>
<td>3.0</td>
</tr>
<tr>
<td>Diamond-water</td>
<td>0.606</td>
<td>0.608</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂CuO₄-water</td>
<td>0.606</td>
<td>0.621</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-water</td>
<td>0.606</td>
<td>0.618</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>SiC-EG</td>
<td>0.253</td>
<td>0.266</td>
<td>5.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Diamond-EG</td>
<td>0.253</td>
<td>0.256</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂CuO₄-EG</td>
<td>0.253</td>
<td>0.262</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-EG</td>
<td>0.253</td>
<td>0.261</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>SiC-PAO</td>
<td>0.137</td>
<td>0.145</td>
<td>5.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Diamond-PAO</td>
<td>0.138</td>
<td>0.140</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂CuO₄-PAO</td>
<td>0.137</td>
<td>0.157</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-PAO</td>
<td>0.137</td>
<td>0.141</td>
<td>2.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

5.4.3 Thermal Conductivity Measurements

Table 5-4 summarizes the results of the thermal conductivity measurements on the twelve Sigma-Aldrich nanopowder-based nanofluids, including base fluid thermal conductivity, nanofluid thermal conductivity, thermal conductivity enhancement percentage, and the enhancement predicted by the Maxwell effective medium theory when no interfacial resistance is included. From the table it can be seen that the Al₂CuO₄-PAO fluid exhibits the largest enhancement at 14.6%. However, it should be noted that the particle loading is also rather high, with a value of 10 wt.%. Furthermore, comparison to the Maxwell model could not be made because the thermal conductivity of Al₂CuO₄ could not be found. The next highest enhancement measured was for the SiC-PAO fluid at 1 vol.%. It was measured as having an enhancement of 5.8%, which is almost two times that predicted by the Maxwell model. Therefore, even though considerable aggregation was observed for this fluid (the
DLS measured average particle size was on the order of microns) this characteristic may prove beneficial for the efficient transport of heat, as hypothesized by Keblinski et al. [53], Wang et al. [70], and Prasher et al. [32]. Because of this promising result, a series of SiC-PAO fluids will be discussed in detail in Section 5.5.

Figure 5-13 plots thermal conductivity enhancement percentage versus infinite shear viscosity enhancement percentage, from which it can be seen that the Al$_2$CuO$_4$-PAO fluid exhibits the most desirable behavior, as it has the highest thermal conductivity enhancement and one of the lowest viscosity enhancements. However, its viscosity enhancement (15.1%) is still larger than its thermal conductivity enhancement (14.6%), and this is at the highest shear rate conducted. Therefore, it should be noted that if an average or mid-shear rate viscosity value was used instead of the infinite shear viscosity, the viscosity enhancement would be much larger than the corresponding thermal conductivity enhancement, and none of the twelve fluids would appear viable for any of the aforementioned real-world applications.
5.5 SiC-PAO Nanofluids

Because the 1 vol.% SiC-PAO fluid exhibited favorable results, it was further examined by creating four other dilutions, one more concentrated sample, and four samples at various concentrations with a surfactant included. Therefore, a total of ten fluids will be discussed in this section. They are SiC-PAO with no surfactant at particle loadings of 0.01, 0.05, 0.1, 0.5, 1.0, and 1.5 vol.%, as well as SiC-PAO with Span 80® as the surfactant at particle loadings of 0.1, 0.5, 1.0, and 1.5 vol.%. The surfactant was present in the four samples at a concentration, relative to the PAO oil, of 5 wt.%, or equivalently 4.07 vol.%.

5.5.1 Nanoparticle Characterization

Along with the DLS measurements conducted on the original 1 vol.% SiC-PAO fluid, detailed in Section 5.4.1, DLS measurements were also performed on the 1 vol.% SiC-PAO-surfactant fluid, from which it was measured that the particles, when dispersed with a surfactant, had an average size of 292.6 nm, which is an order of magnitude less than the size reported for the SiC-PAO fluid. Furthermore, the PDI for the SiC-PAO-surfactant fluid was measured to be 0.191, which is more than 2.5 times smaller than the PDI measured for the SiC-PAO fluid. Therefore, this indicates that while a part of the aggregation occurs prior to dispersion in the PAO, most aggregation happens once the particles are mixed with the PAO.
5.5.2 Rheological Measurements

Rheological testing was conducted on the SiC-PAO and SiC-PAO-surfactant fluids using the AR-G2 rheometer. Figure 5-14 and Figure 5-15 plot viscosity versus shear rate and viscosity versus shear stress, respectively, for the SiC-PAO fluids at the six aforementioned concentrations. From the plots it can be seen that the 0.01 vol.% sample demonstrates Newtonian behavior, while the 0.05 vol.% sample exhibits breakdown of structure due to the increased shearing forces. This structure does not rebuild itself when
the shear rate is decreased, but instead, the fluid behaves Newtonian. For the four higher concentration fluids yield stresses are apparent. Ultimately, for these fluids, as the particle concentration is increased, agglomeration, or structuring occurs to a greater degree, and the force required to break-up this structure also increases.

In order to more thoroughly understand the behavior of these fluids, creep tests were conducted on the 1 vol.% sample. Figure 5-16 plots the results of this test as compliance versus time, from which we can see that for stresses lower than 1.0 Pa, little or no flow is observed, and therefore the yield stress has not been reached. However, at an imposed stress of 1.0 Pa, the sample begins to flow. The viscosity was then calculated for each of the ten imposed stresses by taking the inverse of the slope of the compliance versus time curves. These results are plotted in Figure 5-17(a) along with the results of a steady flow test conducted on the 1.0 vol.% sample, as well as the results of a steady flow test when the sample had been pre-sheared. From the plot we can see that the results from the creep test clearly define a yield stress that has a value in the range of 0.1 to 1.0 Pa. The viscosity during the course of the test decreases from a value of approximately 40,000 Pa·s to the infinite shear viscosity of approximately 0.01 Pa·s.
Figure 5-17: Viscosity versus shear stress for the 1 vol.% SiC-PAO fluid including the results from (a) steady flow testing, creep testing, and steady flow testing after pre-shear, and (b) steady flow testing after pre-shear, steady flow testing immediately following a steady flow test, and steady flow testing in reversed direction (from high shear stress to low shear stress followed by low shear stress to high shear stress).

The steady flow test including pre-shearing was conducted by shearing the sample at 2000 s\(^{-1}\) for 60 seconds, immediately followed by a typical steady flow test. From the results we can see that there is a yield stress to begin with, and that the viscosity decreases as the shear stress is increased. When the shear stress is lowered systematically, the viscosity increases at a slower rate, indicating that nanoparticle structuring was broken-up by the shearing forces. Interestingly enough, this behavior exactly parallels the behavior of the sample when no pre-shearing was implemented, leading one to believe that the nanoparticle structure was not thoroughly broken up by the pre-shearing action.

Figure 5-17(b) plots the results of when a steady flow testing is conducted immediately following a steady flow test, as well as when a steady flow test is conducted in the reverse direction (from high shear stress to low shear stress, followed by low shear stress to high shear stress). From the results we can see when two tests are run back-to-back, this has no effect on the outcome of the second test. However, if the same test is run in the reverse direction there is no break-up of structure. Instead, the viscosities at the
commencement and conclusion of the test are equivalent, and of the same value as the viscosity at the end of the standard steady flow test.

Figure 5-18 plots viscosity versus shear rate and viscosity versus shear stress for the four SiC-PAO-surfactant fluids, from which we can see that the addition of the surfactant drastically decreases the viscosity at the commencement of the test. In particular, for the 1.0 vol.% sample, the viscosity at a shear rate of 0.2 s⁻¹ was decreased by more than two orders of magnitude from 2.944 to 0.0139 Pa·s. The infinite shear viscosity is also decreased by approximately 28%. Furthermore, none of the four fluids exhibit a yield stress. Instead, they appear to be shear thinning, with the degree of shear thinning dependent on the particle concentration.

Figure 5-19 plots infinite shear viscosity versus volume fraction for both the SiC-PAO fluids and the SiC-PAO-surfactant fluids along with the Einstein-Batchelor correlation. As can be seen from the plot, all of the viscosities are greater than that predicted by Einstein-Batchelor, with the exception of the two least concentrated SiC-PAO fluids. Furthermore, for the four most concentrated fluids (1.0 and 1.5 vol.% both with and without surfactant), the fluids without surfactant have viscosities greater than their with-
surfactant counterparts. Lastly, the SiC-PAO-surfactant fluids seem to exhibit a more systematic linear increase in infinite shear viscosity as the concentration is increased.

5.5.3 Thermal Conductivity Measurements

Figure 5-20(a) plots thermal conductivity enhancement percentage versus volume fraction for both the SiC-PAO and SiC-PAO-surfactant fluids, including the Maxwell effective medium theory prediction without interfacial resistance. From the plot it can be
seen that the SiC-PAO fluids exhibit thermal conductivity enhancements in excess of that predicted by Maxwell's theory. In particular, at a concentration of 1.5 vol.% the enhancement measured is almost twice that predicted by Maxwell's Theory. For the SiC-PAO-surfactant fluid it can be seen that the enhancement is even greater. At the maximum concentration of 1.5 vol.% the thermal conductivity enhancement is almost 11%. Furthermore, there is a linearly increasing trend of thermal conductivity enhancement with increased concentration, which does not intercept the y-axis at zero, but instead at a value of about 2.5%. This is due to the fact that the presence of a surfactant increases the thermal conductivity of the base fluid prior to the addition of SiC particles.

Figure 5-20(b) plots thermal conductivity enhancement percentage versus infinite shear viscosity enhancement percentage for both the SiC-PAO and SiC-PAO-surfactant fluids. From the figure we can see that not only does the presence of the surfactant act to increase the thermal conductivity enhancement of the composite, but it also decreases the viscosity enhancement, a desirable effect. However, for all concentrations the viscosity enhancement is still greater than the thermal conductivity enhancement.

5.6 Nano-emulsions

Three water-in-PAO oil emulsions were synthesized according to the procedure detailed in Section 3.1. Span 80® was chosen as the surfactant, and it was mixed with PAO oil at a concentration of 5 wt.%. Water was then added to the PAO oil-surfactant mixture at concentrations of 1, 5, and 10 wt.%, or equivalently, 1.33, 6.94, and 14.7 vol.%. This last step was performed while sonicating the samples with the ultrasonic probe until the input energy had reached 15,000 J.
<table>
<thead>
<tr>
<th>Nano-fluid</th>
<th>DLS-Measured Particle Size (nm)</th>
<th>Polydispersity Index (PDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-in-PAO Oil Emulsion 1.33 vol.%</td>
<td>95.35</td>
<td>0.112</td>
</tr>
<tr>
<td>Water-in-PAO Oil Emulsion 6.94 vol.%</td>
<td>206.1</td>
<td>0.081</td>
</tr>
<tr>
<td>Water-in-PAO Oil Emulsion 14.7 vol.%</td>
<td>262.7</td>
<td>0.202</td>
</tr>
</tbody>
</table>

Table 5-5: Summary of the four nanoparticle powders obtained from Sigma-Aldrich, including the manufacturer stated particle size as well as the concentrations dispersed in water, EG, and PAO oil.

5.6.1 Nano-droplet Characterization

DLS measurements were performed on the three emulsions at the as-synthesized concentration. The results of the testing are summarized in Table 5-5, from which it can be seen that as the concentration of water is increased the droplets tend to coagulate more easily to form larger droplets. Furthermore, it can be noted that the 6.94 vol.% sample can be considered monodisperse because its PDI is less than 0.1. Ultimately, the small droplet size of 9.8 nm achieved by Yang and Han [34] using the same synthesizing method could not be actualized, as the droplets measured were at least an order of magnitude larger.

5.6.2 Rheological Characterization

The AR-G2 rheometer was used to conduct measurements on the three emulsions. Figure 5-21(a) plots viscosity versus shear rate, from which we can see that the two more dilute samples exhibit Newtonian behavior for most of the range and begin to demonstrate hysteresis at low shear rates. The 14.7 vol.% concentration is shear thinning with a larger amount of hysteresis at higher shear rates than the other two samples. Figure 5-21(b) plots the average viscosity versus volume fraction for the three emulsions, along with the Einstein-Batchelor correlation for PAO oil. From the plot we can see that the measured viscosities
increase with increased water concentration, and that the trend is well-predicted by the theory.

### 5.6.3 Thermal Conductivity Measurements

Figure 5-22(a) plots thermal conductivity enhancement percentage versus volume fraction for the three emulsions along with the Maxwell Theory for PAO oil when no interfacial resistance is included. From the plot we can see that the thermal conductivities increase with increased volume fraction, as expected, and that the trend is well-predicted by
the Maxwell model. Figure 5-22(b) plots thermal conductivity enhancement percentage versus viscosity enhancement percentage, from which it can be seen that the viscosity enhancement increases much more rapidly than the thermal conductivity enhancement. This is an undesirable behavior in terms of practical applications, as it would require more power to pump the fluid than would be saved by increased thermal efficiency.
Chapter 6

Conclusions

The major goal of this thesis was to study the rheological and thermal properties of a plethora of nano-structured dispersions in order to gain a more detailed understanding of what traits prove beneficial at increasing the thermal conductivity of a suspension while maintaining a relatively low viscosity. In particular, the dispersion properties examined were nanostructure material, nanoparticle size, base fluid material, nanostructure concentration, and presence of a surfactant.

Chapter 4 reported on the characterization of the dispersed phase as well as the rheological and thermal properties of seven different nanofluids that had been purchased from commercial manufacturers and were composed of both spherical nanoparticles and carbon nanotubes. It was found that the Au-EG fluid was the only one that exhibited a thermal conductivity enhancement in excess of that predicted by the Maxwell effective medium theory (~6% enhancement at a concentration of 0.3 vol.%). It was further discovered that the reason for this enhancement was due to the presence of ~6.7 vol.% water in the as-received high concentration sample which not only increased the effective thermal conductivity of the sample, but also reduced the viscosity. Furthermore, the Al₂O₃-EG sample received from the same company exhibited similar features. In particular, its viscosity decreased appreciably with increased nanoparticle characterization, opposite to
what is expected and predicted by the Einstein-Batchelor correlation. Because of this anomalous behavior, this fluid exhibited a positive thermal conductivity enhancement while also maintaining a negative viscosity enhancement, a beneficial behavior. However, as with the Au-EG sample, it was hypothesized that these desirable properties were due to the presence of water in the as-received high concentration sample.

Furthermore, all six of the fluids containing spherical nanoparticles that were discussed in this chapter demonstrated Newtonian or slight shear thinning behavior with increased shear rate. The seventh fluid, namely MWCNTs dispersed in water, exhibited the unusual presence of a yield stress. It was hypothesized that the existence of a yield stress was due to the formation of a network structure among the MWCNTs at high shear rates, which acted to appreciably increase the viscosity of the sample. Testing demonstrated that the undesirable network structure could be reduced by sonicating the fluid prior to testing. At low concentrations of dispersed nanotubes yielding did not occur. Instead, the fluid behaved in a Newtonian manner and had a viscosity similar to that of the base fluid, water.

Chapter 5 reported on the characterization of the dispersed phase as well as the rheological and thermal properties of nineteen different nanofluids that had been fully- or partially-synthesized at MIT and were composed of spherical nanoparticles, graphene sheets, fullerenes, and nano-droplets. The largest thermal conductivity enhancement was measured for the Al$_2$CuO$_x$-PAO as being 14.6%. However, the viscosity enhancement for this fluid was still greater than the thermal conductivity enhancement, and this was at a particularly high nanoparticle loading of 10 vol.%. A thermal conductivity enhancement of 8.9% was measured for the SiC-PAO fluid at a concentration of only 1.5 vol.%. This enhancement is almost twice as much as that predicted by the Maxwell effective medium theory. With the addition of a surfactant, the thermal conductivity enhancement of the SiC-PAO-surfactant
fluid was measured to be 11.9% at 1.5 vol.%, two percentage points greater than its non-surfactant counterpart.

Several of the fluids discussed in this chapter exhibited yield stresses that could be attributed to the formation of a network structure of aggregated nanoparticles, much like the aforementioned MWCNTs. However, as was demonstrated by the SiC-PAO fluid, the addition of a surfactant helps to keep the nanoparticle from clustering to the same degree, thereby eliminating the presence of a yield stress, and reducing the viscosity of the fluid over the entire range of shear rates. Furthermore, since the addition of a surfactant also increases the thermal conductivity of the fluid, this combination of improved heat transfer and decreased viscosity is highly desirable for “real world” applications.
Appendix

There is significant confusion in the field of nanofluids regarding the correct citation of the origin of the effective medium theory for composites. As can be seen from such literature written by Prasher et al. [32], Nan et al. [56], Wang et al. [70], as well as several others, these authors have given credit to Maxwell-Garnett in labeling the effective theory as the Maxwell-Garnett model, or equivalently, the M-G or MG model. Wang et al. [70] has even gone so far as to cite an article by J.C. Maxwell-Garnett entitled, “Colours in metal glasses and in metallic films” as the original publication of the well known effective medium theory. The mistake is explained by the fact that there are two different men with similar names.

The first man, named James Clerk Maxwell, was the famous physicist who lived from 1831 to 1879 and published the well known *Treatise on Electricity and Magnetism* in the late 1800’s [92]. He did so with the help of what seemed to be his friend William Garnett (1850-1932) who is listed as the editor on the 1881 publication of Maxwell’s *An Elementary Treatise on Electricity*. Furthermore, the preface of the book indicates that while most of the book was written by James Clerk Maxwell, he died before publication, requiring the editor, William Garnett, to organize and finalize his work. Therefore, it is possible that, in referring to this seminal work by Maxwell, several authors cited in this thesis may label it as the Maxwell-Garnett Theory.
However, the confusion is further exacerbated by the fact that William Garnett named his son James Clerk Maxwell Garnett (our second man) in honor of his friend James Clerk Maxwell. Maxwell Garnett, as he was commonly known, lived from 1880 to 1958 and was an educationalist and peace campaigner [93]. He is the author of the aforementioned article, “Colours in metal glasses and in metallic films.” This article contains no mention of any effective medium theory, and does not even contain a single equation.

Therefore, following suit of several papers that correctly cite Maxwell’s contribution, i.e. Choi [1] and Xue [61], in writing this thesis I have labeled it the Maxwell model.
Bibliography


