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The Effect of Nanoparticle Agglomeration on Enhanced Nanofluidic Thermal Conductivity

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ABSTRACT

The study and understanding of the enhanced thermal conductivity of nanofluids is a relatively young and growing research area. Thus far sample characterization at this scale, especially for *in situ* properties, has been incomplete and not well defined. Without adequate sample description capabilities, progress in understanding and ultimately realizing the full potential of enhanced nanofluidic thermal conductivity will be hampered. Presented here are thermal conductivity measurements, using the transient hot wire method, of samples prepared by systematic variation of both ultrasonication time and pH for alumina nanoparticle solutions. A marked shift in enhanced thermal conductivity relative to the carrier fluid alone is observed. The working hypothesis that the prevention of particle agglomeration leads to improved thermal conductivity is supported by *in situ* effective particle size distribution measurements using dynamic light scattering methods.

1. INTRODUCTION

1.1 Nanofluid Heat Transfer Potential

In the past decade, a great deal of research has been focused on the emerging field of nanofluid heat transfer. Nanofluid is a term used to describe fluid suspensions that contain nanometer-scale solid particles. It has long been recognized that adding solid particles to a fluid would, by virtue of their superior heat transfer capability, increase the thermal conductivity of the composite fluid as shown in Ahuja (1975). In 1988, Liu *et al.* (1988) proposed that suspending nanometer-scale particles in heat transfer fluids could substantially increase thermal transport more effectively than larger-scale particles. The first experimental study on this possibility came in 1993 by Masuda *et al.* (1993). Since that time, numerous experimental studies by Choi (1995), Xuan (2000), Eastman *et al.* (2001), Xie *et al.* (2002a,b,c), and Das (2003) have determined that nanofluids can not only remain stable indefinitely, but also boost thermal conductivity values far in excess of theoretical predictions. However, considerable ambiguity remains when interpreting these results due to inconsistencies in nanofluid preparation and size characterization. The accepted theoretical models that accurately predict thermal transport in composite fluids containing larger particles appear to be particularly at odds with experimentation that has shown the clear trend for thermal enhancement to increase as temperature increases or particle diameter decreases.

1.2 Theoretical Understanding

The preliminary theoretical work in the field was conducted by Maxwell (1904) over a century ago. His theories treat composite fluids as stationary dispersions whose properties depend only on their volume fraction loading.

More recently, the work of Hamilton and Crosser (1962) treat heat transfer in composite fluids as a function of particle surface area. These two theoretical models predict the properties of composite fluids containing larger particles quite well, but fail to predict the anomalous thermal conductivity increases seen in the most recent nanofluid research. Most notably, they contain no functional dependence on particle size or fluid temperature, two parameters that have repeatedly been shown to affect thermal conductivity in experimentation. Discrepancies between previous theory and recent research have led to a new generation of thermal conductivity models which have a dependence on particle size and/or temperature. The work of Keblinski *et al.*⁶ suggests four possible mechanisms as the most likely to play a role in the anomalous thermal conductivity observed in nanofluids: liquid layering at the particle interface, Brownian motion of the particles, ballistic heat transport in nanoparticles, and particle clustering. These four mechanisms form the basis of most nanofluid heat transfer models. Yu and Choi (2003), Xue (2004), and Wang (2003) have all proposed theories that depend on the existence of semi-crystalline layers of liquid molecules that are thought to develop at the particle/fluid interface. Jang and Choi (2004) have alternatively proposed a model based primarily on the Brownian motion of individual particles and “microconvection” currents that result from such motion. Clearly, high quality experimental data is needed for comparison with the many proposed theoretical approaches. The validation and acceptance of any of these models requires systematic study of thermal conductivity enhancement over a wide range of well characterized nanoparticles sizes. Such a project, however, rapidly runs into the problem of adequately characterizing the suspension stability and dispersion. The size of particles within a nanofluid depends not only on the original size of the nanoparticles, but also the degree to which clumping and agglomeration effects are present within the nanofluid suspension. To date, nanofluids have been prepared by two different methods, a single step approach where nanoparticles are dispersed directly into a carrier fluid as part of their synthesis as seen in Eastman *et al.* (2001), and two step methods where pre-formed nanoparticles are purchased and separately combined with fluid. The single step method is superior from a stability standpoint, because it eliminates the possibility of large clumps forming while the nanoparticles are in their dry powder form. On the other hand, the recent boom in commercial nanoparticle availability allows for the relatively simple acquisition of nanopowders of widely ranging particle size, making a two-step process much more desirable from an experimental standpoint. The use of a two-step process, however, necessitates additional processing in order to ensure complete dispersion of particles within the fluid. When a two-step process is used, it is inevitable that some degree of clumping and agglomeration takes place between individual nanoparticles when they are stored and shipped in dry bulk form. Subjecting a nanofluid sample to ultrasonic energy is commonly used to break apart any pre-existing clumps. Acids and additional surfactants are also commonly added to nanofluids to help stabilize the suspension once nanoparticles have been added. Colloidal science indeed predicts that nanofluids are particularly prone to clumping because of their extraordinarily high number densities, and indicates that the pH and electrolyte concentration of nanofluids have pronounced effects on the stability of nanosystems. The effects of electrolyte concentration are outlined in Kallay and Žalac (2002). Accordingly, the details of nanofluid preparation are expected to play an important role in the individual particle sizes of the resulting fluid, and hence affect the thermal conductivity. This work reports the systematic study of how the nanofluid preparation parameters of pH and added ultrasonication energy affect the thermal conductivity enhancement of nanofluid samples.

1.3 Size Characterization Difficulties

The inherent difficulties associated with characterizing the particle size and dispersion characteristics of nanofluids further complicate the study of heat transport in these suspensions. The nanometer-scale of the particle additions dramatically limits the options available for sample characterization. Electron microscopy techniques are by far the most commonly available methods to image nano-size objects. Traditional electron microscopes, however, require a nanofluid sample to be dried before it can be imaged in a vacuum. Therefore, additional agglomeration resulting from the drying process (as well as clumping structures that might be destroyed in the process) would tend to render the results as non-representative. In addition, the resulting images also represent a very small snapshot of the fluid, and therefore, many carefully chosen samples are required to ensure data is representative of the entire sample. Alternative methods include “wet-cell” electron microscopy where images are taken of samples that remain in solution, small angle x-ray diffraction scattering (SAXS), and dynamic light scattering (DLS). The latter two options are particularly attractive because they can provide full particle size distribution data that is representative of the entire sample. Although, for SAXS some concerns include an upper cut off on detectable size and possible interaction effects. In this work a combination of size characterization methods are used: standard TEM to determine the size and shape of the individual dry nanoparticles, and DLS to provide particle size distribution data for prepared nanofluids.

2. EXPERIMENTAL PROCEDURE

2.1 Nanofluid Preparation

For this study, nanofluid samples were prepared using a two step method. Nanoparticles of $\gamma\text{-Al}_2\text{O}_3$, obtained in dry powder form from Nanophase Technologies Corporation, having a manufacturer-specified average particle diameter of 47nm were mixed into a base fluid to yield several precisely measured particle volume fractions. For the purposes of this study, deionized water was chosen as an appropriate base fluid. The desired amount of nanoparticles was added to the base fluid while continuously agitating the mixture with a magnetic mixer. The resulting nanofluid was then placed in a Cole-Parmer 130-Watt ultrasonic processor to break apart any agglomerations of nanoparticles. The time and total power output of the ultrasonication process were systematically varied to observe their effect on thermal conductivity. The sonication process resulted in a large increase in sample temperature, particularly for longer sonication times. To account for this, all samples were carefully transferred to a temperature controlled test cell and cooled to room temperature prior to data acquisition. A pair of thermocouples in the test cell were then used to ensure a steady and consistent temperature throughout the sample. All thermal conductivity measurements were taken at a temperature of 22°C.

2.2 Thermal Conductivity Measurement

In order to measure the thermal conductivity of nanofluid samples, a measurement device based on the transient hot wire (THW) technique was constructed. To avoid any electrical conduction through the test fluid, the insulated hot wire method developed by Nagasaka and Nagashima (1981) was used. Briefly, our apparatus passes an electrical current through a thin (25 μm diameter) platinum wire that is suspended vertically within a cylinder containing the test fluid. The applied electrical current serves to rapidly heat the wire, which in turn dissipates heat to the surrounding fluid. As the thin platinum wire changes temperature, its electrical resistance also changes according to a well-defined relationship based on material properties of platinum. By measuring the electrical resistance of the platinum element, the temperature of the wire was precisely determined. The repetition rate of the instrumentation was 6 times per second. For relatively low applied power values and consequently lower temperatures of the platinum wire, natural convection in the cell is avoided and the thermal conductivity of the fluid can be calculated if one considers conductive heat transport from an infinite line source only. The resulting function depends on the applied electrical power per unit length, q , and the measured slope of the linear wire temperature vs. $\ln(t)$ relationship where t represents the elapsed time since initiation of the heat source. This relation is given as equation (1) below.

$$k = \frac{q}{4\pi(\text{slope}(\ln(t), T))} \quad (1)$$

For each sample, data acquisition was taken for a duration of 35 seconds, after which data from between 1 and 4 seconds was used to calculate the slope of the temperature vs. log time plot. This period of time was chosen to avoid any effects of nonuniformities in the wire insulation at very short times and natural convection cells that develop at long elapsed times. The apparatus and data collection method were carefully verified using pure water and 99+% pure ethylene glycol.

3. RESULTS

3.1 Dry Nanoparticle Size

Independent measurement of the average size of dry nanoparticles was undertaken using TEM imagery and a SAXS method. TEM microscopy confirmed that in their dry state the nanoparticles are spherical in nature. Analysis of the micrographs also provided an estimated average particle size of 58.8nm in diameter. Small angle x-ray scattering measurements produced an average diameter value of 44.2nm ($\pm 2.7\%$). These measurements correspond closely to

the supplier claim of 47nm average particle diameter. The supplier used the Brunauer-Emmett-Teller (BET) method to derive the particle size to an estimated accuracy of 3%.

3.2 Sonication Time Variation

The following data depicts the thermal conductivity enhancement of 2% Al_2O_3 nanofluids as functions of isolated preparation parameters. Nanofluid samples were prepared using Nanophase 47nm Al_2O_3 particles suspended in a base fluid of deionized water. Samples were prepared according to the production procedure described earlier.

Figure 1 depicts the thermal conductivity enhancement of nanofluids as a function of time subjected to ultrasonication at a fixed energy level of 4W. Here, thermal conductivity enhancement is presented as the ratio of nanofluid thermal conductivity divided by the thermal conductivity of the base fluid, in this case deionized water. All samples had an unmodified pH value of 4.6 that is characteristic of Al_2O_3 /deionized water nanofluids.

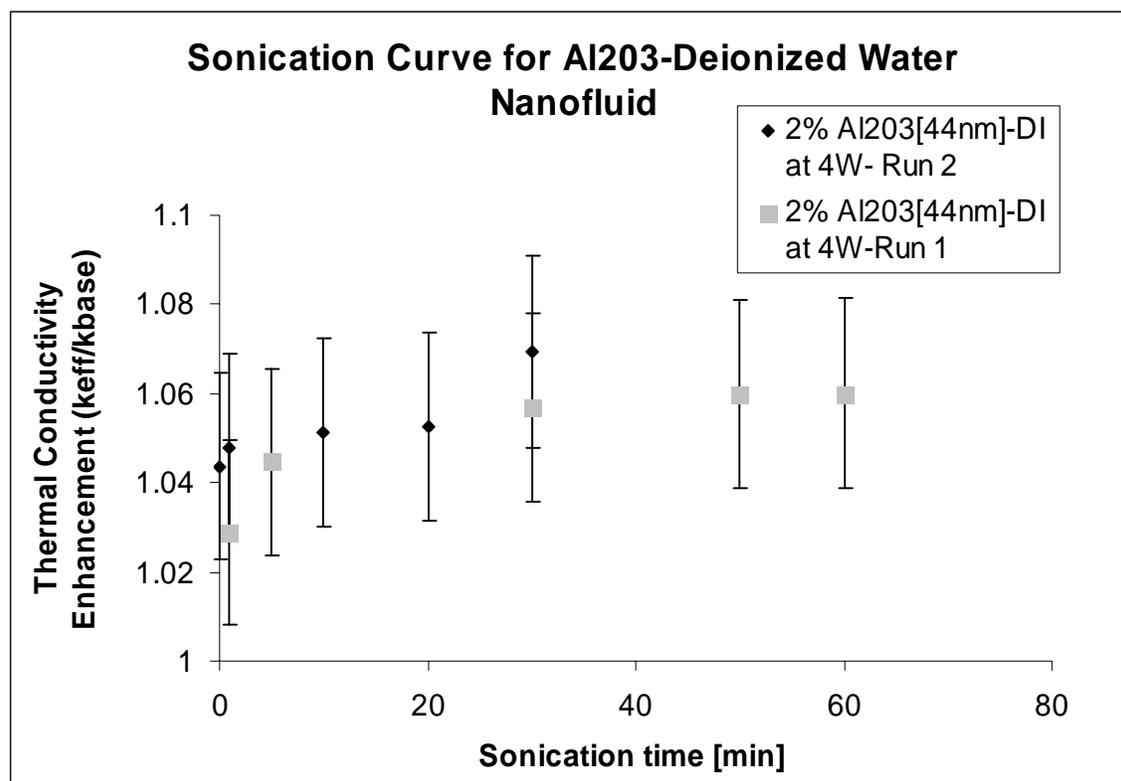


Figure 1: The thermal conductivity enhancement of alumina nanofluid as a function of sonication time at 4W

3.3 pH Variation

Figure 2 shows the results from a similar systematic variation of pH while the parameter of the total ultrasonication energy delivered to the sample is held constant. The pH values of the resulting nanofluid samples were altered by the addition of HCl to the base fluid prior to nanoparticle addition. Electrolyte concentration and pH are known to be important variables in the dispersion of larger colloids and are therefore expected to affect the dispersion of nanoparticles as well. All samples were subjected to ultrasonic energy of 4 watts for one minute before testing.

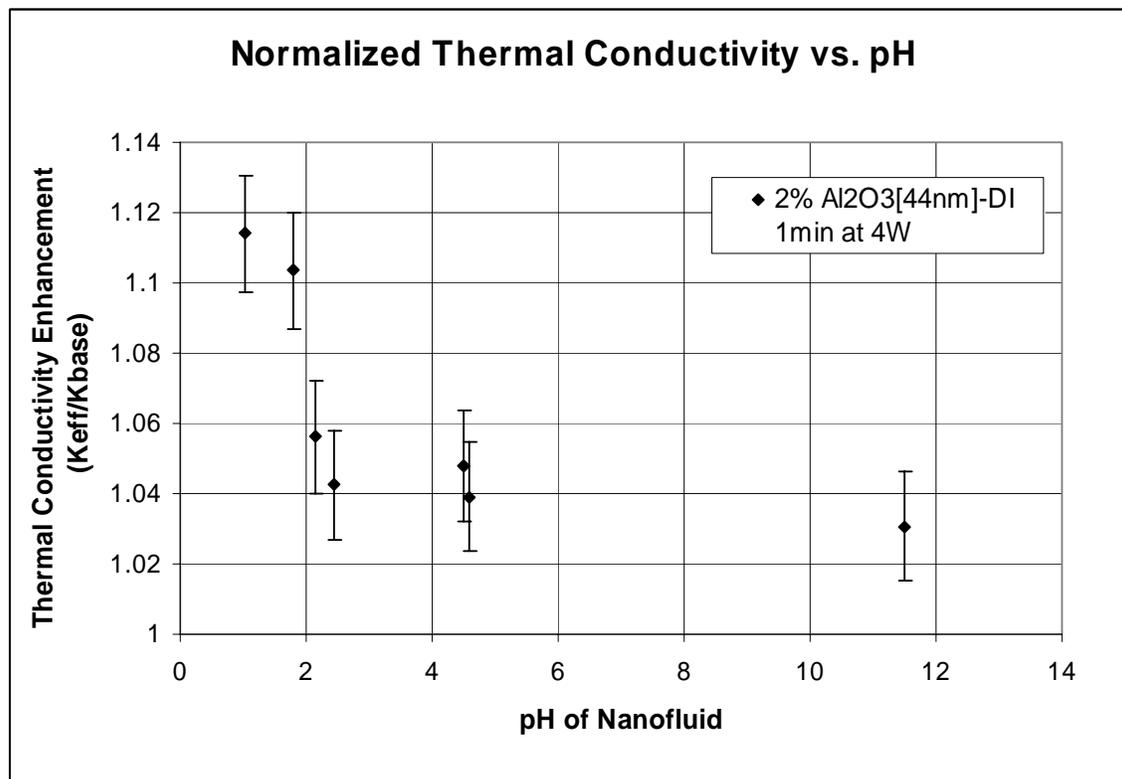


Figure 2: The thermal conductivity enhancement of alumina nanofluid as a function of its pH value

3.4 DLS Particle Size Measurement

Figure 3 shows an experimentally determined particle size distribution for nanofluids prepared identically to those exhibiting the highest thermal conductivity enhancement. The figure shows two identically prepared nanofluids with a pH of 1.04 after HCl was added to the base fluid. The data depicted was obtained from the RGS Scientific company using a Nanotracs particle analyzer working on the principals of dynamic light scattering. The two curves represent results from identically prepared fluids from two separate data runs.



Figure 3: Size distribution of particles in 2% Al_2O_3 nanofluids prepared using 1 minute ultrasonication at 4W in a base fluid of 1ml HCl and 50ml DI water (0.353 molarity HCl, pH 1.04)

4. DISCUSSION

4.1 Functional Dependence on Preparation

Systematically varying the preparation parameters of ultrasonic time and pH are shown to have clear effects on the thermal conductivity of nanofluids. Figure 1 clearly depicts a functional dependence of nanofluid thermal conductivity on the duration of ultrasonication used to produce the nanofluid. Longer durations of ultrasonic energy are shown to result in larger thermal conductivity enhancement while holding the temperature constant. According to previous experimental results thermal conductivity enhancement tends to increase in smaller particle nanofluids. Accordingly, the presented results imply that effectively smaller particles are present in nanofluids that have been subjected to increased ultrasonic energy due to a decrease in the size of particle clumps that exist within the suspension. Figure 2 shows a similar functional dependence depending on the pH of the nanofluid. As applied to colloids, DLVO theory predicts that the higher electrolyte concentrations present in low pH fluids would help stabilize separate particles and lead to increased dispersion. Drastic thermal conductivity enhancement values were determined at very low pH indicating that smaller particles are present in nanofluids prepared in that fashion. The experimental results presented in figure 2 therefore indicate increased dispersion of nanoparticles correlates with large electrolyte concentrations. Both the ultrasonication data and the pH data indirectly suggest that a reduction in effective particle size leads to a noticeable increase in measured thermal conductivity. It remains then to confirm that variations in these two preparation techniques lead to a change in effective particle size. Efforts are ongoing to provide this verification. Preliminary size distribution data from the parameters that seem to yield the best thermal conductivity enhancement presented in figure 3 confirms that even at very low pH, the majority of particles within the nanofluid are significantly larger than the size of single particles in their dry state. The dry particle size was repeatedly measured to be around 44-58nm, and yet the peak particle size detected in solution was about 110nm. It is worth noting that the DLS measurements were taken completely *in situ* and represent an average of the entire sample. Therefore, it is clear that even for the nanofluid samples exhibiting the best thermal conductivity enhancement obtained in our experiments, the present dispersal methods failed to produce single-particle dispersion where every nanoparticle is independent within the fluid. It also seems that the present experimental results are not actually characteristic of 47nm particles in solution, but rather 110nm particles.

5. CONCLUSION

The present investigation strongly indicates that the preparation technique used to produce nanofluids can have a large effect on their resultant thermal conductivity values. The lack of nanoparticle dispersion within nanofluids appears to be a limiting factor in the effectiveness of their heat transfer. Agglomeration issues must be overcome in order to obtain the full potential of nanofluid heat transfer. Furthermore, any attempts to match experimental data with proposed theory must take into account the fact that effective nanoparticle size within a nanofluid appears to differ significantly from the size of the same nanoparticles in their dry state. Agglomeration and size characterization issues are current limitations to the usefulness and understanding of nanofluids.

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