Enhancement of Thermal Transport in Water and Ethylene Glycol Using Al_2O_3 Nanoparticles

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Abstract

Current research demonstrates a significant increase in the thermal conductivity of suspensions containing small volume fractions (<5%) of metal or metal oxide nanoparticles compared with the base liquids alone. Due to incomplete discussion of sample preparation and characterization in a significant portion of literature to date, there is some ambiguity in what the published data actually represents. This paper provides thermal conductivity measurements for two types of nanofluids, Al_20_3-deionized water and Al_20_3-ethylene glycol, with a well described sample preparation method. The nanofluids were loaded at 2% by volume with 44 nm Al_20_3 nanoparticles. Thermal conductivity values were measured using the transient hot wire (THW) method, the nanoparticle size was obtained by small angle X-ray scattering (SAXS), and the morphology was determined by transmission electron microscopy (TEM).

1. Introduction

In recent years many articles have been published analyzing the enhancement of thermal transport in fluids containing suspended metal and metal oxide nanoparticles [1, 2]. Mechanisms of heat transfer that could explain the observed enhancement have been formulated and presented, but there is still no definitive agreement between the various theoretical expectations and experimental results. Possible reasons for this observed disagreement could be associated with the way nanoparticle suspensions were prepared and characterized in the experiments.

The effectiveness of nanoparticles in a base fluid to enhance its thermal transport properties depends on agglomeration properties of the suspended solids in the mixture [3]. It is therefore desirable to systematically control the agglomeration of nanoparticles within test nanofluids.

Most experiments conducted to date have utilized some kind of ultrasonic agitation to disperse nanoparticles suspended in base fluids and thus to ensure that there is no significant agglomeration [2]. Within the literature, however, the specifics of the sonication procedure, i.e., power and duration, actually used in the sample preparation are rarely listed [4, 5]. This oversight results in the reporting of experimental findings that could be misleading since they are associated with nanofluid samples of known bulk average composition but of unknown structure on a smaller scale. It amounts to an unknown variable (perhaps effective particle size) when analyzing thermal transport mechanisms.

As an example of the demonstrated dependence of thermal conductivity on sonication parameters through agglomeration control, in a recent paper by Hong et al. [1] an increase of 18% in thermal conductivity was observed for Fe-ethylene glycol nanofluid, with the only varying parameter being the duration of the sonication for the sample. This finding shows that all documentation of experiments in which sonication is a step in nanofluid processing needs to include information on the sonication parameters and the justification for them in order for the results obtained to be most useful. The need for justifying the sonication parameters used should be stressed because they have been presented inconsistently in the literature. Some authors who state the time duration and power of the sonication process have used significantly different sonication parameters even though they were processing nanofluids of similar composition. Moreover, their parameters were frequently not comparable to the values recommended by manufacturers of ultrasonic processors. For example, manufacturer-recommended sonication time is usually in the range of several minutes[1], while researchers have sonicated their nanofluids anywhere from fractions of hours [6] to several hours [2].

Characterization techniques for dispersed nanoparticles, as done in most relevant experiments to date, could also be connected to the observed difference between the theoretical expectations and experimental results. The method most often used to characterize dispersed nanoparticles has been transmission electron microscopy (TEM). This method is used not only to determine size distribution of the nanoparticles in the suspension, but also to check for the possible formation of agglomerates. The validity of this method should be questioned considering that TEM samples are small as compared with the entire batch of test solutions used in the experiment and the fact that they must be dried before characterization. Thus, the researchers assume that agglomerate structures do not change as they are removed from a fluid, dried, and placed in a vacuum. However, that assumption has not yet been confirmed experimentally.

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2. Experimental

2.1 Nanoparticle characterization

For this experiment, the γ-Al_2O_3 nanoparticles used were purchased from a commercial company (Nanophase Technologies Corporation, Romeoville, IL). The average size of the nanoparticles was given by the supplier as 47 nm, but was independently measured by one of the authors using the small angle X-ray scattering (SAXS) method.

The SAXS procedure is a well-established method of investigating the properties of colloidal suspensions, and it is capable of measuring structures on the nanometer scale [7]. In this technique, X-rays transmitted through a sample exhibit scattering behavior when they come into contact with any electron density variations such as those present at the solid/liquid interface between nanoparticles and the carrier fluid. Scattered X-rays are captured by detectors at discrete points along a range of scattering angles. From those detectors, an experimental scattering curve $I_{exp}(q)$ is obtained, where the scattering intensity is plotted as a function of the scattering vector, q. Equation (1) gives the scattering vector as a function of scattering angle, 2θ,- and X-ray wavelength, λ.

$$q = \frac{4\pi \sin(\theta)}{\lambda} \tag{1}$$

The carrier fluid contribution to the experimental scattering curve is removed from $I_{exp}(q)$ by subtracting a scattering curve obtained for the fluid alone. The resulting nanoparticle scattering curve is then fit to a theoretical distribution that yields values for the average particle radius of gyration and the average particle shape factor.

In this experiment the TEM investigation determined the particle shape to be roughly spherical (figure 1). Average particle diameter was determined from the radius of gyration assuming all nanoparticles were spherical in shape. Note that the most significant feature of the SAXS method, in contrast to TEM, is that it can characterize the whole sample in situ in less time than other microscopy techniques.

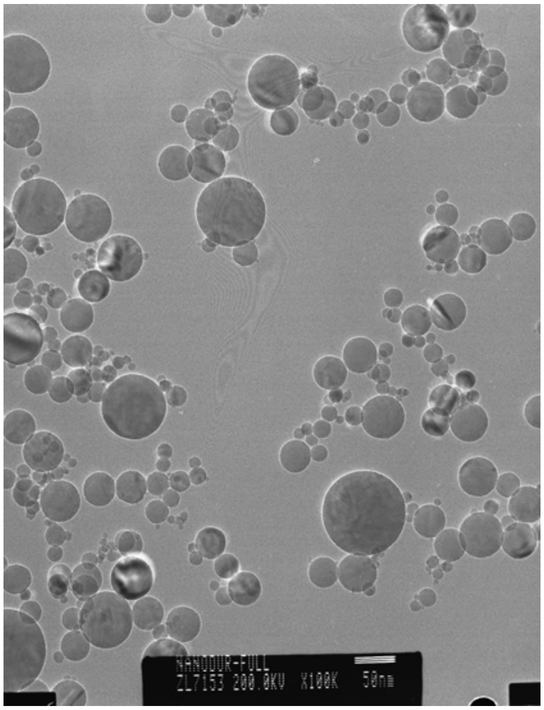

Figure 1. TEM picture of a 0.2 % by weight loaded nanofluid. It can be seen that the nanoparticles have a spherical morphology.

2.2 Nanofluid preparation

To prepare the nanofluids with a specific volume-fraction loading of Al_2O_3 nanoparticles, a precision balance was used to weigh samples. The particles were then mixed with the two base fluids, deionized water and reagent-grade (99+%) ethylene glycol. 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 agglomerations of nanoparticles. The time and power of sonication 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 ($22 \pm 0.5^{o}C$) prior to data acquisition. Two thermocouples placed axially on each end of the test cell were then used to ensure a steady and consistent temperature throughout the sample. Unless otherwise noted, all thermal conductivity measurements presented here were taken at a temperature of $22 \pm 0.5^{o}C$.

2.3 Thermal Conductivity Measurement

A custom-built device based on the transient hot wire (THW) technique was used to measure the thermal conductivity of each nanofluid sample. To avoid any electrical conduction through the test fluid, an insulated wire (3 µm, Isonel™ insulation) was used as described by Nagasaka and Nagashima [8]. The apparatus passes an electrical current through a thin, 25 μm diameter platinum wire that is suspended vertically in a cylindrical cell filled with the test mixture. The applied electrical current rapidly heats the wire, which in turn dissipates heat to the surrounding fluid at a rate that depends on thermal properties of the mixture. As the thin platinum wire changes temperature, its electrical resistance also changes in accordance with a well characterized formula [9]:

$$R(T) = R_o(1+\alpha T) \tag{2}$$

where $R(T)$ is the wire resistance, R_o is the wire resistance at 0 ˚C, T is the wire temperature, and α is the characteristic constant for platinum. Note that the α value for the wire is 0.00391 $^\circ C^{-1}$. By considering the electrical resistance of the platinum element, the temperature of the wire is measured six times per second using the Agilent-34970A data acquisition unit. For relatively low applied power values, convection in the cell is avoided and the temperature change of the wire is dependant only on the rate of applied electrical energy and the thermal conductivity of the fluid. This relation is given by a specific solution to Fourier's law for the boundary conditions associated with an infinitely long, infinitely thin, power source suspended in an infinite cylinder of fluid. The resulting expression is given as equation (3), where α is the thermal diffusivity of the fluid, k is the thermal conductivity of the fluid, ΔT is the change in temperature of the fluid, q is power input per unit length of wire, R is radius from the center of the cylinder, t is elapsed time, and ln(C) is Euler's constant.

$$\Delta T(R,t) = \frac{q}{4\pi k}\ln\left(\frac{4\alpha t}{R^2 C}\right) \tag{3}$$

Substituting R for the radius of the wire and taking the derivative of equation (1) with respect to ln(t) gives equation (4).

$$\frac{d\Delta T}{d\ln(t)} = \frac{q}{4\pi k} \tag{4}$$

Since applied power and thermal conductivity are assumed to be constant, this transforms into a workable equation as given below:

$$k = \frac{q}{4\pi(S)} \tag{5}$$

where S is the slope of the ΔT versus ln(t) curve.

In practice, the plot of ΔT versus ln(t) does deviate from the expected linear form due to a number of physical effects. At very short elapsed times the heat from electrical resistance heating of the wire will not yet have reached the surrounding fluid. The heat must pass outward through the 3 μm thick electrical insulation layer on the Pt wire, which has a different thermal conductivity value than the surrounding liquid. This effect is estimated to last about 1 microsecond, and should not greatly affect any more than the first data point. In addition, the linearity of the plot will degrade after long elapsed times due to the onset of thermal convection in the fluid.

A constant power of 0.80 W/m was applied to the wire in each thermal conductivity measurement. The resulting ΔT versus ln(t) data collected between elapsed times of 1s and 3.5s were then fitted with a linear trend line whose slope was applied to equation (4). The preceding process was validated on base fluids alone and showed excellent correlation with known thermal conductivity values. The error associated with the apparatus is estimated to be below 2%.

3. Results and discussion

The independent measurement of nanoparticle size using the SAXS method produced an average diameter value of 44.2 nm (± 2.7%) as compared with the average size value of 47 nm reported by the supplier. The apparent difference in the measured values is likely to have been caused by utilization of two different measuring techniques and samples from two different batches. The supplier used the Brunauer-Emmett-Teller (BET) method to derive the particle size with an accuracy of 3%.

Initially, several nanofluid samples were prepared in deionized water with 2% Al_2O_3 (44 nm) loading by volume. The sonication time of the samples was varied from 0 to 60 minutes at 4 W. The resulting thermal conductivity enhancement values (k_{nano} / k_{base}) of the samples are shown in figure 2. A rise in thermal conductivity is evident as the sample sonication time increases. Assuming that increased sonication time does indeed decrease the agglomeration of nanoparticles in a sample, the data indicate that breaking up nanoparticle clumps in a nanofluid increases its k_{nano}. Notably, thermal conductivity values were found to level off after approximately 50 minutes of sonication at this power level. The value for optimum sonication time is consistent with the results obtained by Hong et al. [1] even though power input and the nanofluid composition were significantly different in that experiment. However, we did not, observe as high of an increase in thermal conductivity with variation of sonication time as Hong et al. [1]. In their case, the increase in k_{nano} was around 18% while in this experiment it was approximately 3% for the water-based nanofluid and zero for the ethylene glycol suspension. Most likely reason for this large difference in the relative increase of k_{nano} is that the particles used by Hong et al. were smaller. For smaller particles, agglomeration is more pronounced, and relative sonication effects on thermal conductivity can thus be more significant than in suspensions with larger nanoparticles. It is interesting to note, however, that Hong et al. did not mention any use of a temperature control for their nanofluids even though they sonicated their samples at high power and performed measurements immediately after the sonication. The increase they observed might also be attributable in part to the temperature effects discussed in [2].

Two experimental runs were performed from different batches of nanoparticles purchased from the same supplier. The measurements of thermal conductivity for the two runs differ only at low sonication times, suggesting a difference in the level of agglomeration between the two nanoparticle batches. This difference is probably due to small variations between the processing and storage conditions used for the two samples.

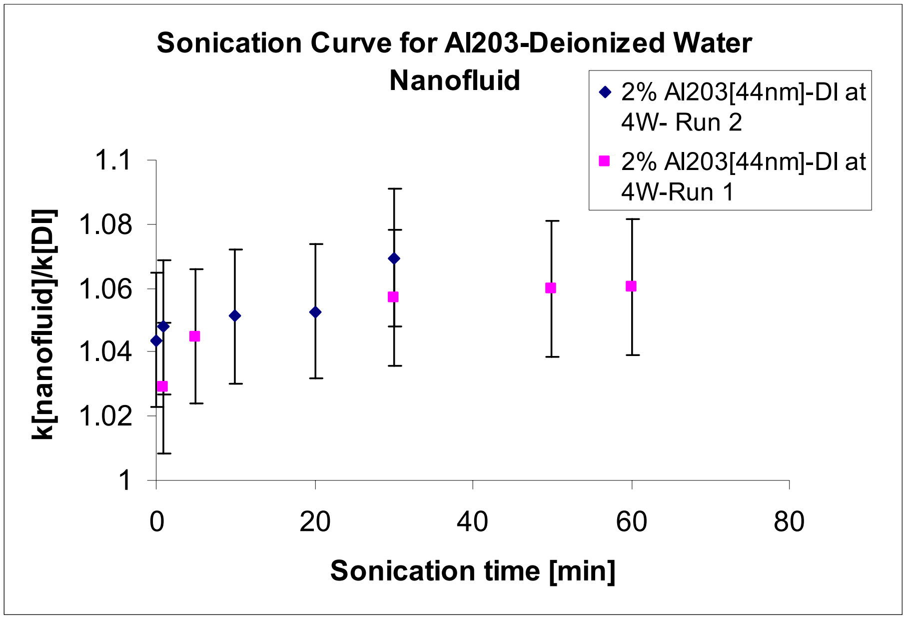

Figure 2. Sonication data for Al_20_3-deionized water nanofluid.

Figure 3 shows sonication data for a 2% volume-loaded Al_2O_3-ethylene glycol nanofluid at two different power settings of the ultrasonic processor. The values of thermal conductivity seem not to have been affected by the different applied power, and they appear to be independent of the sonication time. This is a slightly different behavior than that observed for water-based nanofluid measurements. For water at the same particle loading there was some increase in thermal conductivity with an increase in duration of sonication. The observed behavior might be caused by polarity differences between the two fluids, where nanoparticles are better dispersed in the more polar fluid, ethylene glycol, than in less polar deionized water. This type of a relation could be analyzed further by varying the zeta potential of the nanoparticles, with the pH for example, in the two base fluids and analyzing the results. A related experiment was conducted by Kwak et al [10], where optimal parameters for sonication were determined through the relation of zeta potential and the stability of the suspension.

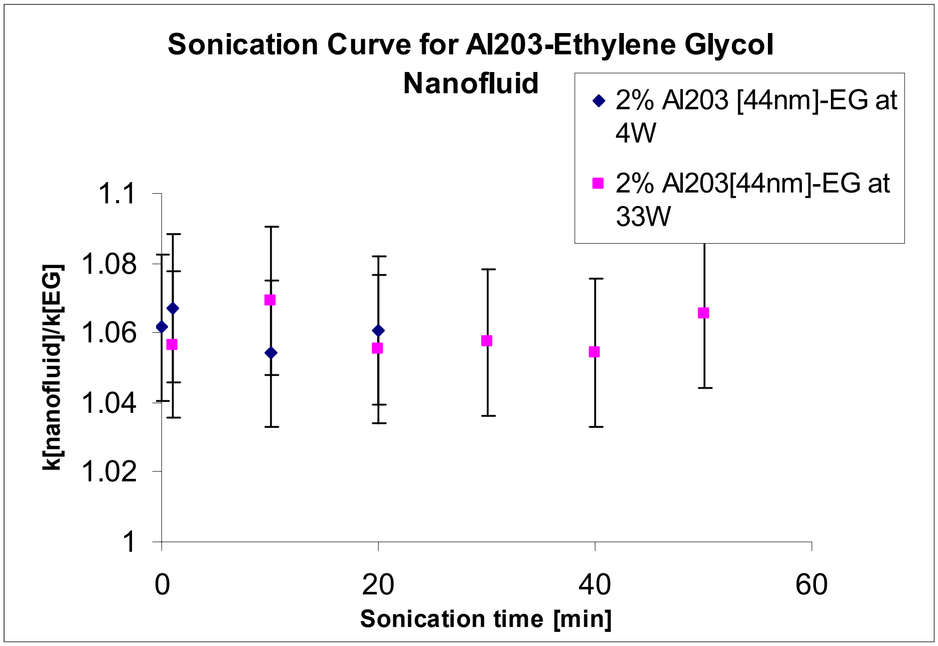

Figure 3. Sonication data for Al_20_3-ethylene glycol nanofluid.

4. Conclusion

The focus of this experiment was to determine effects of sonication time and power on the stability of nanofluids with respect to their thermal conductivity values. Figures 2 and 3 summarize the relation between sonication time, power, and the thermal conductivity obtained in this research. From the data obtained it can be concluded that a 2% volume-loaded ethylene glycol nanofluid requires no sonication (4W and 33 W) to reach stability while a nanofluid based on deionized water requires sonication (4W) for at least 50 minutes. In these regimes thermal conductivity is independent of sonication and the nanofluid can be viewed as stable, with a constant but probably very small level of nanoparticle agglomeration. This information would be essential for any experiment in which thermal transport is to be analyzed for these kinds of nanofluids because the agglomeration variable would be known to stay constant.

SAXS method for determining nanoparticle size was tried as an alternative to the more common TEM method. No supporting information was found to specifically prove or disprove the validity of TEM in characterization of suspended agglomerations, but it seems more valid to use a method for which there is no ambiguity about whether the sample used in the experiment is of the same structure as that being characterized.

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