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Effects of aggregation on the thermal conductivity of alumina/water nanofluids

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ABSTRACT

Nanofluids display enhanced heat transfer properties, and several mechanisms, including Brownian motion and aggregation of the suspended particles, have been proposed to explain this enhancement. Agreement on a unified understanding of the mechanism has yet been reached. The role of particle aggregation is particularly controversial, and requires further study. Thus, this work analyzes the effects of particle aggregation on the thermal conductivity of alumina/water nanofluids. The thermal conductivity of the nanofluids was measured using the 3ω method by varying the aggregation state until gelled nanofluids are formed. Brownian motion and sedimentation effects could thereby be removed from the analysis. The viscosity of the nanofluids was measured to quantify the aggregation state. The alumina/water nanofluids showed non-Newtonian characteristics in the low shear rate regime. The thermal conductivity could be explained by the classical Maxwell effective medium theory. High aggregation in the gel state produced large enhancements in the nanofluid thermal conductivity.

1. Introduction

Nanofluids are colloidal suspensions of nanoparticles in a base fluid, and they have attracted substantial attention as highly efficient heat transfer fluids. Several physical mechanisms, including particle Brownian motion [1–3], the presence of an ordered molecular layer around each particle [4–6], and aggregation and clustering of the particles [7–9], have been proposed to explain the anomalously enhanced heat transfer. However, the disparate mechanisms have not yet been reconciled [10–19]. Eapen et al. [20,21] recently concluded that thermal conduction in nanofluids is classical in nature, based on a comparison of the thermal conductivity of various nanofluids with classical Maxwell theory [22,23]. They pointed out that previous nanofluid studies paid attention only to the lower Maxwell bound for well-dispersed particles in a base fluid. By considering the upper Maxwell bound for linear or chain-like particle configurations, most nanofluid thermal conductivity measurements were found to lie between the upper and lower bounds of the EMT, and no anomalous heat transfer enhancement was observed. Aggregation, which is responsible for high thermal conductivities in nanofluids at the upper bound, has become an important issue.

The effects of particle aggregation on thermal conduction in nanofluids have been studied extensively both theoretically and experimentally [7–9,13,14]. A consensus has not yet been reached as to whether aggregation contributes to enhanced thermal transport. Some studies report thermal conduction enhancement by aggregation [7–9], but the opposite trend has also been observed [13,14]. It is important to realize that sedimentation of the aggregates may affect the results. Particle aggregation can increase aggregate size, and aggregates larger than a critical size threshold tend to settle under the force of gravity.

Recently, Shalkevich et al. [24] measured the thermal conductivity of silica/ and alumina/water nanofluids in fluid, glass, and gel states, and they revealed that heat diffusion in nanofluids was significantly affected by the particle arrangements. The thermal conductivity of a gelled sample formed from a network of contacting particles was slightly larger than that of the fluidic samples. On the other hand, the thermal conductivity of glassy samples, in which particles were separated and kinetically frozen by strong repulsive interparticle forces, was lower than that of the base fluid, and the thermal conductivity decreased rapidly with decreasing particle volume fraction. These results, particularly the properties of the gelled nanofluid, provided insight into the mechanism of heat transfer in nanofluids because the gelled sample represents an extreme state of aggregation. In this regards, the objective of this work was to investigate the thermal conductivity of fluidic and gelled alumina/water nanofluids over a wide range of aggregation states by varying the volume fraction and electrolyte concentration in the nanofluids. Because previous studies examined gelled samples prepared at a single electrolyte concentration [24], this work clarifies the relationship between the aggregation state of a nanofluid and its effective thermal conductivity. Alumina/water nanofluids were selected for analysis because they show a relatively large enhancement in thermal conductivity. Silica/water nanofluids are more stable than alumina/water nanofluids at high volume

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fractions, but the thermal conductivity enhancement is relatively small due to the low thermal conductivity of silica. It should be noted that gelled nanofluids present two advantages. First, particles in a gel state stick together to form static networks of particles, which avoid sedimentation. Second, particle Brownian motion is suppressed in the networks.

In this work, the thermal conductivity of fluidic and gelled alumina/water nanofluids was measured using the 3ω method [25–27] at various alumina volume fractions (1, 3, and 5 vol.%) and NaCl concentrations (0.05 and 0.5 M). The thermal conductivity was compared with predictions from the classical effective medium theories [22,23,28–30]. To examine the rheological characteristics of the alumina/water nanofluid as well as to quantify the aggregation state, the viscosity was also measured over a wide range of shear rates using a parallel plate rheometer. Viscosity is a critical material property that determines the utility of a nanofluid for certain industrial applications. In contrast with thermal conductivity, less attention has been paid to the rheological behavior of alumina/water nanofluids.

2. Effective medium theory

The Maxwell EMT has been widely used to analyze the thermal conductivity properties of nanofluids [20–23]. The early Maxwell model agrees well with the experimental results at low particle volume fraction only. However, Hashin and Shtrikman [23] derived the Maxwell (H–S) bounds using variational principles without any restriction on the volume fraction. The theory includes lower and upper bounds that depend on the geometrical configurations of the suspended spherical particles. At the lower bound, nanoparticles are well-dispersed, and the base fluid corresponds to a continuous phase. At the upper bound, the nanoparticles form a continuous phase with linear or chainlike particle configurations, and the base fluid becomes a dispersed phase. Once the thermal conductivity of the nanoparticle exceeds that of the base fluid ($\kappa_p > \kappa_{bf}$), the Maxwell bounds for the thermal conductivity of the nanofluid are expressed by

$$\kappa_{bf}\left[1+\frac{3\varphi(\kappa_p-\kappa_{bf})}{3\kappa_{bf}+(1+\varphi)(\kappa_p-\kappa_{bf})}\right]\le\kappa_{nf}\le\kappa_p\left[1-\frac{3(1-\varphi)(\kappa_p-\kappa_{bf})}{3\kappa_p-\varphi(\kappa_p-\kappa_{bf})}\right],\tag{1}$$

where κ and φ are the thermal conductivity and volume fraction, respectively. The subscripts *bf*, *nf*, and *p* represent the base fluid, nanofluid, and nanoparticle, respectively.

The Bruggeman model (BGM) [28] is also used to describe the effective thermal conductivity of a binary mixture containing well-dispersed spherical particles:

$$\varphi\left(\frac{\kappa_p-\kappa_{nf}}{\kappa_p+2\kappa_{nf}}\right)+(1-\varphi)\left(\frac{\kappa_{bf}-\kappa_{nf}}{\kappa_{bf}+2\kappa_{nf}}\right)=0.\tag{2}$$

The solution to Eq. (2) is [29]

$$\kappa_{nf}=\frac{1}{4}[(3\varphi-1)\kappa_p+(2-3\varphi)\kappa_{bf}]+\frac{\kappa_{bf}}{4}\sqrt{\Delta},\tag{3}$$

where

$$\Delta=(3\varphi-1)^2\left(\frac{\kappa_p}{\kappa_{bf}}\right)^2+(2-3\varphi)^2+2(2+9\varphi-9\varphi^2)\left(\frac{\kappa_p}{\kappa_{bf}}\right).\tag{4}$$

The Hamilton Crosser (HC) model [30] is another model for describing liquid–solid mixtures containing well-dispersed non-spherical particles. The HC model considers the effects of the particle shape by introducing a shape factor n as follows,

$$\frac{\kappa_{nf}}{\kappa_{bf}}=\frac{\kappa_p+(n-1)\kappa_{bf}-(n-1)\varphi(\kappa_{bf}-\kappa_p)}{\kappa_p+(n-1)\kappa_{bf}+\varphi(\kappa_{bf}-\kappa_p)}.\tag{5}$$

The shape factor n is set to be 3 for spheres.

The Maxwell bounds, BGM, and HC model were computed using Eqs. (1), (3)–(5) for alumina/ and silica/water nanofluids prepared at volume fractions up to 6% (Fig. 1). Thermal conductivity values used for the calculation were as follows; water: 0.61 W m^{-1} K^{-1}, alumina: 33 W m^{-1} K^{-1}, and silica: 1.4 W m^{-1} K^{-1} [31]. Because the thermal conductivity of alumina was much larger than that of silica, the gap between the upper and lower Maxwell bounds was much wider for the alumina/water nanofluid than for the silica/water nanofluid. The BGM and HC model ($n = 3$) predictions for well-dispersed particles lay slightly above the lower Maxwell bounds.

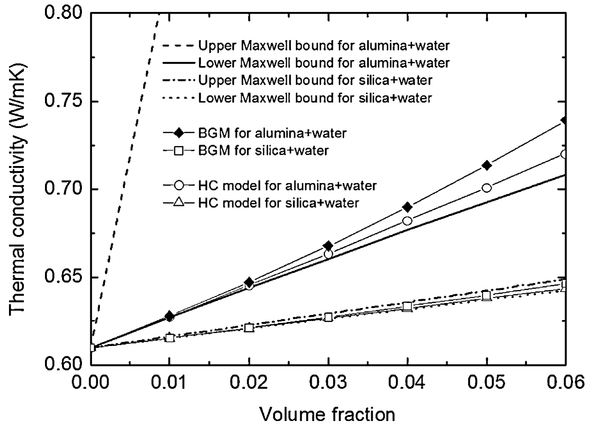

Fig. 1. Theoretical models for the alumina/ and silica/water nanofluids.

3. Experimental

3.1. Preparation of the nanofluids

A commercially available alumina/water nanofluid (Alfa Aesar, Al_2O_3 colloidal dispersion 12733) was used in the experiment. According to the product specifications, the alumina particles were suspended in water in a mass fraction of 20%, which corresponded to a volume fraction of 5%. The solution was diluted with additional DI water to form 1 vol.% and 3 vol.% nanofluids. A nominal size of the particles was 50 nm and the alumina existed as pseudo-boehmite with chemical composition corresponding to γ-AlO(OH) or $Al_2O_3{\cdot}H_2O$. The particles were positively charged, and the pH of the nanofluid samples was pH 4 at 25 °C, which was not particularly sensitive to dilution (<2%).

Addition of an electrolyte to a colloid reduces the thickness of the electrical double layer on a particle surface and weakens the repulsive forces between particles. As a result, particles aggregate to create a gel state [24]. In this work, aggregation of the alumina nanofluid was induced by a 5 M NaCl solution. The NaCl solution was gradually added to the nanofluids with stirring to achieve uniform mixing. The final concentrations of NaCl were 0.05 or 0.5 M for each sample (1, 3, and 5 vol.% alumina). The 3 and 5 vol.% samples gelled at both 0.05 M and 0.5 M NaCl concentrations. Whereas 1 h was required for nanofluid gelation at 0.05 M, at 0.5 M, the sample gelled within 5 min. Unlike the high-concentration samples, the 1 vol.% nanofluid did not form a gel at any electrolyte concentration, which was believed to be due to an insufficient particle population. After adding the electrolyte, we waited 24 h for the sample to form a stable gel structure before measurements of the properties.

3.2. TEM imaging

High-resolution scanning transmission electron microscopy (HR-STEM, JEM-2200FS, JEOL) was conducted to examine the aggregation state of the sample. The HR-STEM samples were prepared by diluting the nanofluid with DI water, transferring the dilute sample to a TEM grid, and drying the grid at room temperature.