

# Thermal Conductivity of Nanoparticle-Fluid Mixture

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**Effective thermal conductivity of mixtures of fluids and nanometer-size particles is measured by a steady-state parallel-plate method. The tested fluids contain two types of nanoparticles,  $\text{Al}_2\text{O}_3$  and  $\text{CuO}$ , dispersed in water, vacuum pump fluid, engine oil, and ethylene glycol. Experimental results show that the thermal conductivities of nanoparticle-fluid mixtures are higher than those of the base fluids. Using theoretical models of effective thermal conductivity of a mixture, we have demonstrated that the predicted thermal conductivities of nanoparticle-fluid mixtures are much lower than our measured data, indicating the deficiency in the existing models when used for nanoparticle-fluid mixtures. Possible mechanisms contributing to enhancement of the thermal conductivity of the mixtures are discussed. A more comprehensive theory is needed to fully explain the behavior of nanoparticle-fluid mixtures.**

## Nomenclature

$c_p$	= specific heat
$k$	= thermal conductivity
$L$	= thickness
$Pe$	= Peclet number
$\dot{q}$	= input power to heater 1
$r$	= radius of particle
$S$	= cross-sectional area
$T$	= temperature
$U$	= velocity of particles relative to that of base fluids
$\alpha$	= ratio of thermal conductivity of particle to that of base liquid
$\beta$	= $(\alpha - 1)/(\alpha - 2)$
$\gamma$	= shear rate of flow
$\rho$	= density
$\phi$	= volume fraction of particles in fluids

## Subscripts

$e$	= effective property
$f$	= base fluid property
$g$	= glass spacer
$p$	= particles
$r$	= rotational movement of particles
$t$	= translational movement of particles

## I. Introduction

IN recent years, extensive research has been conducted on manufacturing materials whose grain sizes are measured in nanometers. These materials have been found to have unique optical, electrical, and chemical properties.<sup>1</sup> Recognizing an opportunity to apply this emerging nanotechnology to established thermal energy engineering, it has been proposed that nanometer-sized particles could be suspended in industrial heat transfer fluids such as water, ethylene glycol, or oil to produce a new class of engineered fluids with

high thermal conductivity.<sup>2</sup> Because the thermal conductivities of most solid materials are higher than those of liquids, thermal conductivities of particle-fluid mixtures are expected to increase. Fluids with higher thermal conductivities would have potentials for many thermal management applications. Because of the very small size of the suspended particles, nanoparticle-fluid mixtures could be suitable as heat transfer fluids in many existing heat transfer devices, including those miniature devices in which sizes of components and flow passages are small. Furthermore, because of their small sizes, nanoparticles also act as a lubricating medium when they are in contact with other solid surfaces.<sup>3</sup>

Heat transfer enhancement in a solid-fluid two-phase flow has been investigated for many years. Research on gas-particle flow<sup>4-7</sup> showed that by adding particles, especially small particles in gas, the convection heat transfer coefficient can be greatly increased. The enhancement of heat transfer, in addition to the possible increase in the effective thermal conductivity, was mainly due to the reduced thickness of the thermal boundary layer. In the processes involving liquid-vapor phase change, particles may also reduce the thickness of the gas layer near the wall. The particles used in the previous studies were on the scale of a micrometer or larger. It is very likely that the motion of nanoparticles in the fluid will also enhance heat transfer. Therefore, more studies are needed on heat transfer enhancement in nanoparticle-fluid mixtures.

Thermal conductivities of nanoparticle-fluid mixtures have been reported by Masuda et al.,<sup>8</sup> Artus,<sup>9</sup> and Eastman et al.<sup>10</sup> Adding a small volume fraction of metal or metal oxide powders in fluids increased the thermal conductivities of the particle-fluid mixtures over those of the base fluids. Pak and Cho<sup>11</sup> studied the heat transfer enhancement in a circular tube, using nanoparticle-fluid mixtures as the flowing medium. In their study,  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2$  were dispersed in water, and the Nusselt number was found to increase with the increasing volume fraction and Reynolds number.

In this work,  $\text{Al}_2\text{O}_3$  and  $\text{CuO}$  particles measuring approximately 20 nm are dispersed in distilled (DI) water, ethylene glycol, engine oil, and vacuum pump fluid. Thermal conductivities of the fluids are measured by a steady-state parallel-plate technique. Several theoretical models for computing effective thermal conductivity of composite materials are used to explain the thermal conductivity increase in these fluids. Results obtained from the calculations are compared with the measured data to evaluate the validity of the effective thermal conductivity theories for liquids with nanometer-size inclusions. Other possible microscopic energy transport mechanisms in nanoparticle-fluid mixtures and the potential applications of these fluids are discussed.

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## II. Measurement of Thermal Conductivity of Nanoparticle-Fluid Mixtures

Two basic techniques are commonly used for measuring thermal conductivities of liquids, the transient hot-wire method and the steady-state method. In the present experiments, the one-dimensional, steady-state parallel-plate method is used. This method produces the thermal conductivity data from the measurement in a straightforward manner, and it requires only a small amount of liquid sample.

Figure 1 shows the experimental apparatus, which follows the design by Challoner and Powell.<sup>12</sup> The fluid sample is placed in the volume between two parallel round copper (99.9% purity) plates, and the surface of the liquid is slightly higher than the lower surface of the upper copper plate. The surface of the liquid can move freely to accommodate the thermal expansion of the liquid. Any gas bubbles are carefully avoided when the cell is filled with a liquid sample. The cross-sectional area of the top plate is 9.552 cm<sup>2</sup>. The two copper plates are separated by three small glass spacers with a thickness of 0.9652 mm each and a total surface area of 13.76 mm<sup>2</sup>. To control the temperature surrounding the liquid cell, the liquid cell is housed in a larger cell made of aluminum. The top copper plate is centered and separated from the inside wall of the aluminum cell. Holes of 0.89-mm diameter are drilled into the copper plates and the aluminum cell. E-type thermocouples (nickel-chromium/copper-nickel) are inserted into these holes to measure the temperatures. The locations of the thermocouples in the top and lower copper plates are very close to the lower surface of the upper plate and to the upper surface of the lower plate. Because the thermal conductivity of copper is much higher than that of the liquid, these thermocouples provide temperatures at the surfaces of the plates. A total of 14 thermocouples are used.

In this work, although the absolute value of thermal conductivity is to be measured, there is no need to obtain the absolute temperature. It is more important to measure accurately the temperature increase of each thermocouple and to minimize the difference in temperature readings when the thermocouples are at the same temperature. It was found that the accuracy in measuring the temperature increase is better than 0.02°C. The differences in the thermocouple readings are recorded when the thermocouples are at the same temperature in a water bath and are used as calibration values in later experiments.

During the experiment, heater 1 provides the heat flux from the upper copper plate to the lower copper plate. Heater 4 is used to maintain the uniformity of the temperature in the lower copper plate. Heaters 2 and 3 are used to raise the temperature of the aluminum cell to that of the upper copper plate to eliminate convection and radiation losses from the upper copper plate. Therefore, input powers to all of the heaters need to be carefully adjusted. During all measurements, the temperature difference between the upper copper plate and the inside wall of the aluminum cell is less than 0.05°C, and the temperature uniformity in the top and the bottom copper plates is better than 0.02°C. The temperature difference between the two copper plates varies between 1 and 3°C.

All of the heat supplied by heater 1 flows through the liquid between the upper and the lower copper plates. Therefore, the overall thermal conductivity across the two copper plates, including the effect of the glass spacers, can be calculated from the one-dimensional

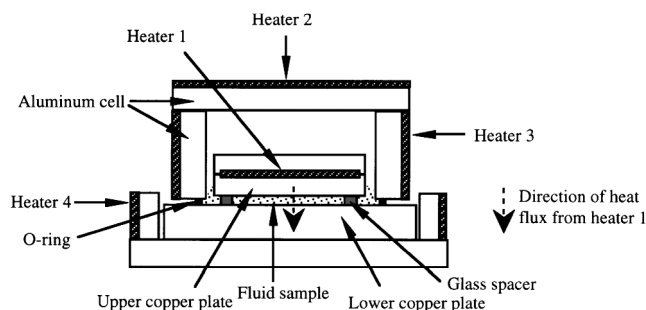


Fig. 1 Experimental apparatus.

heat conduction equation relating the power  $\dot{q}$  of heater 1, the temperature difference  $\Delta T$  between the two copper plates, and the geometry of the liquid cell as

$$k = (\dot{q} \cdot L_g) / (S \cdot \Delta T) \quad (1)$$

where  $L_g$  (0.9652 mm) is the thickness of the glass spacer between the two copper plates and  $S$  (9.552 cm<sup>2</sup>) is the cross-sectional area of the top copper plate. The thermal conductivity of the fluid can be calculated as

$$k_e = \frac{k \cdot S - k_g \cdot S_g}{S - S_g} \quad (2)$$

where  $k_g$  (1.4 W/m · K) and  $S_g$  are the thermal conductivity and the total cross-sectional area of the glass spacers, respectively.

Experimental error is estimated by comparing the measured thermal conductivity of DI water and ethylene glycol with the published data.<sup>13</sup> The absolute error for the thermal conductivities of both fluids is less than  $\pm 3\%$ .

The thermal conductivity of liquid changes with temperature. When a small temperature difference between the two copper plates is used, then the effect of the temperature variation is small. Using the thermal conductivity data of water, it is estimated that the maximum measurement uncertainty in this work caused by the temperature variation across the liquid cell is 0.5%.

## III. Experimental Results

Nanometer-size Al<sub>2</sub>O<sub>3</sub> and CuO powders are obtained from Nanophase Technology Company (Burr Ridge, Illinois). The average diameter of the Al<sub>2</sub>O<sub>3</sub> powders ( $\gamma$  phase) is 28 nm, and the average diameter of the CuO powders is 23 nm. The as-received powders are sealed and are dry and loosely agglomerated. The powders are dispersed into DI water, vacuum pump fluid (TKO-W/7, Kurt J. Lesker Company, Clairton, Pennsylvania), ethylene glycol, and engine oil (Pennzoil 10W-30). The powders are blended in a blender for one-half an hour and then are placed in an ultrasonic bath for another half an hour for breaking agglomerates. A number of other techniques are used to disperse the powders in water and will be described later. The volume fraction of the powder in liquid is calculated from the weight of the dry powder and the total volume of the mixture. Absorption of water vapor could occur when the powders are exposed to air just before placing the powders into fluids; however, the exposed surface of the powders is much smaller than the total surface of the powders. The error caused by water absorption in determining the volume fraction is negligible.

Samples using water, pump fluid, or engine oil as the base fluid are stable when the volume fraction is less than 10%. No agglomeration is observed for a number of weeks (at room temperature). When the volume fraction is greater than 10%, the fluid becomes flocculated in the dispersion process. Samples using ethylene glycol as the base fluid are stable up to a volume fraction of 16%. Unless otherwise noted, samples are prepared without adjusting the pH value.

Results of the thermal conductivity of Al<sub>2</sub>O<sub>3</sub> dispersions at the room temperature (297 K) are shown in Fig. 2a. Figure 2b shows the ratios of the thermal conductivity of the mixture  $k_e$  to the thermal conductivity of the corresponding base fluid  $k_f$ . For all of the fluids, the thermal conductivity of the mixture increases with the volume fraction of the powder. However, for a given volume fraction, the thermal conductivity increases are different for different fluids. The increases in ethylene glycol and engine oil are the highest, whereas that in the pump fluid is the lowest, about half of that in ethylene glycol and engine oil. The effective thermal conductivity of ethylene glycol increases 26% when approximately 5 vol% of Al<sub>2</sub>O<sub>3</sub> powders are added, and it increases 40% when approximately 8 vol% of Al<sub>2</sub>O<sub>3</sub> powders are added. Figures 3a and 3b show thermal conductivities of CuO dispersions in water and in ethylene glycol. For both fluids, thermal conductivity ratio increases with the volume fraction with the same linearity.

To examine the effect of different sample preparation techniques, Al<sub>2</sub>O<sub>3</sub> powders are dispersed in water using three different techniques. Mechanical blending (method 1), coating particles with

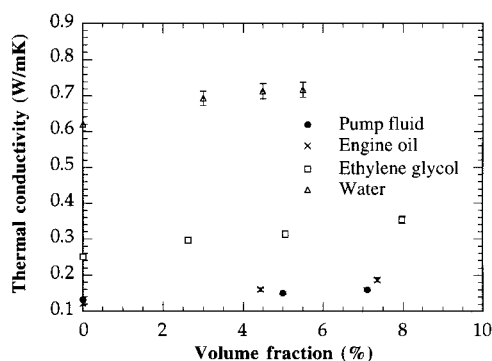


Fig. 2a Thermal conductivity as a function of volume fraction of Al<sub>2</sub>O<sub>3</sub> powders in different fluids.

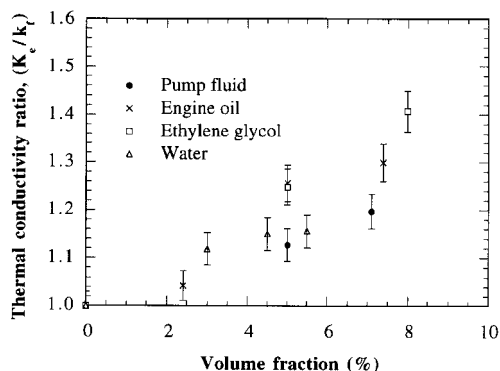


Fig. 2b Thermal conductivity ratio as a function of volume fraction of Al<sub>2</sub>O<sub>3</sub> powders in different fluids.

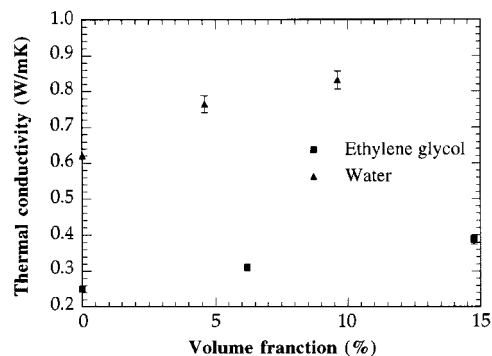


Fig. 3a Thermal conductivity as a function of volume fraction of CuO powders in ethylene glycol and water.

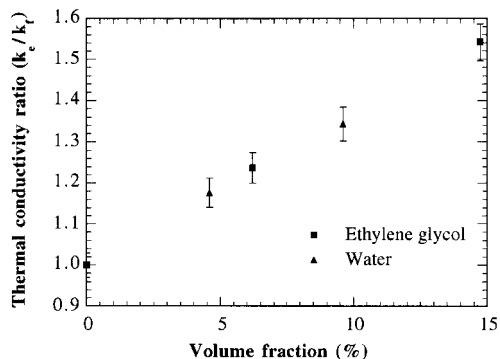


Fig. 3b Thermal conductivity ratio as a function of volume fraction of CuO powders in ethylene glycol and water.

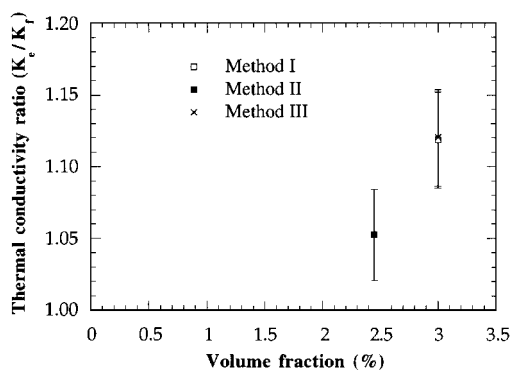


Fig. 4 Thermal conductivity of Al<sub>2</sub>O<sub>3</sub>-water mixtures prepared by three different methods.

polymers (method 2), and filtration (method 3) are used. Method 1, used for preparing all of the samples described earlier, employs a blending machine and an ultrasonic bath. The resulting solutions contain both separated individual particles and agglomerations of several particles. Particles with diameters larger than 1  $\mu\text{m}$  also exist among the as-received powders and, therefore, also in the solution made by method 1. For method 2, polymer coatings (styrene-maleic anhydride,  $\sim 5000$  mol wt, 2.0% by weight) are added during the blending process to keep the particles separated. The pH value must be kept at 8.5–9.0 to keep the polymer fully soluble; therefore, ammonium hydroxide is added. In method 3, filtration is used to remove particles with diameters larger than 1  $\mu\text{m}$ . The calculation of the volume fraction of the particles has taken into account the reduction of the particle volume due to the removal of large particles. Thermal conductivities of these Al<sub>2</sub>O<sub>3</sub>-water solutions are shown in Fig. 4. As for the sample prepared by method 2, its thermal conductivity is compared with that of the fluid with the same volume fraction of polymers and base, which is about 2% lower than that of DI water. The decrease in thermal conductivity due to the addition of polymers is smaller than the measurement uncertainty because the volume concentration of the polymer is small. From Fig. 4, it is seen that the solution made with method 3 has the greatest thermal conductivity increase (12% with 3 vol% particles in water), but that it is still lower than the thermal conductivity increase when the same volume fraction of Al<sub>2</sub>O<sub>3</sub> is dispersed in ethylene glycol.

#### IV. Discussion

In this section, thermal conductivities of nanoparticle-fluid mixtures measured in this work are first compared with experimental data reported in the literature. Effective thermal conductivity theories in the literature are used to compute the thermal conductivity of the mixtures. Results calculated from the effective thermal conductivity theories are compared with the measured data. Other possible transport mechanisms and potential applications of nanoparticle-fluid mixtures are discussed.

##### A. Comparison of Present and Earlier Experimental Data

The results shown in Figs. 2 and 3 differ from the data reported in the literature. For example, Masuda et al.<sup>8</sup> reported that Al<sub>2</sub>O<sub>3</sub> particles at a volume fraction of 3% can increase the thermal conductivity of water by 20%. Lee et al.<sup>14</sup> obtained an increase of only 8% at the same volume fraction, whereas the increase in the present work is about 12%.

The mean diameter of Al<sub>2</sub>O<sub>3</sub> particles used in the experiments of Masuda et al.<sup>8</sup> was 13 nm, that in the experiments of Lee et al.<sup>14</sup> was 38 nm, and that in the present experiments was 28 nm. Therefore, the discrepancy in thermal conductivity might be due to the particle size. It is possible that the effective thermal conductivity of nanoparticle-fluid mixtures increases with decreasing particle size, which suggests that nanoparticle size is important in enhancing the thermal conductivity of nanoparticle-fluid mixtures.

Another reason for the significant differences is that Masuda et al.<sup>8</sup> used a high-speed shearing dispenser (up to approximately

20,000 rpm). Lee et al.<sup>14</sup> did not use such equipment and, therefore, nanoparticles in their fluids were agglomerated and larger than those used by Masuda et al.<sup>8</sup> In the present experiments, the techniques used to prepare the mixtures are different from those used by Masuda et al.<sup>8</sup> and Lee et al.<sup>14</sup> This comparison, together with the data shown in Fig. 4, shows that the effective thermal conductivity of nanoparticle-fluid mixtures depends on the preparation technique, which might change the morphology of the nanoparticles. Also, in the work of Masuda et al.,<sup>8</sup> acid (HCl) or base (NaOH) was added to the fluids so that electrostatic repulsive forces among the particles kept the powders dispersed. Such additives, although low in volume, may change the thermal conductivity of the mixture. In this work, acid or base are not used in most of the samples (except the one with polymer coatings) because of concerns of corrosions by the acid or base.

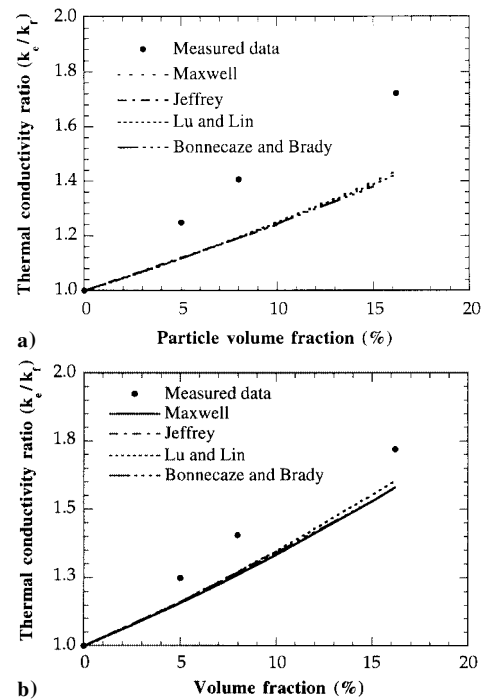
### B. Comparison of Measured Thermal Conductivity of Nanoparticle-Fluid Mixtures with Theoretical Results

Thermal conductivities of composite materials have been studied for more than a century. Various theories have been developed to compute the thermal conductivity of two-phase materials based on the thermal conductivity of the solid and the liquid and their relative volume fractions. Here, the discussions are focused mainly on the theories for statistically homogeneous, isotropic composite materials with randomly dispersed spherical particles having uniform particle size. Table 1 summarizes some equations frequently used in the literature.<sup>15–20</sup> Maxwell's equation,<sup>15</sup> shown in Table 1, was the first theoretical approach used to calculate the effective electrical conductivity of a random suspension of spherical particles. Because of the identical mathematical formulations, computations of electrical conductivity of mixtures are the same as computations of thermal conductivity, dielectric constant, and magnetic permeability. Maxwell's results are valid for dilute suspensions, that is, the volume fraction  $\phi \ll 1$ , or, to the order  $O(\phi^1)$ . A second-order formulation extended from the Maxwell's result was first developed by Jeffrey<sup>16</sup> and later modified by several authors. No higher-order formulations have been reported. Bonnacaze and Brady's numerical simulation<sup>19,20</sup> considered far- and near-field interactions between multiple particles. They showed that for random dispersions of spheres, their simulation results agreed with Jeffrey's equation<sup>16</sup> up to a volume fraction of 20%, whereas Maxwell's equation<sup>15</sup> gave results within 3% of their calculation for a conductivity ratio  $\alpha = 10$  and within 13% when  $\alpha = 0.01$ , up to a volume fraction of 40%. For high-volume fractions ( $\phi > 60\%$ ), the theoretical equations are generally not applicable because the near-field interactions among particles that produce a larger  $k_e$  at high-volume fractions are not considered.

The equations in Table 1 have been successfully verified by experimental data for mixtures with large particles and low concentra-

tions. The difference between the measured data and the prediction is less than a few percent when the volume fraction of the dispersed phase is less than 20% (Ref. 20). The experimental data in the comparison included those obtained by Turner<sup>21</sup> on the electrical conductivity of 0.15-mm or larger solid particles fluidized by aqueous sodium chloride solutions and those obtained by Meredith and Tobias<sup>22</sup> on electrical conductivity of emulsions of oil in water or water in oil with droplet sizes between 11 and 206  $\mu\text{m}$ . Therefore, these effective thermal conductivities can accurately predict the thermal conductivity of particle-fluid mixtures when the particle size is larger than tens of micrometers.

The effective thermal conductivity equations shown in Table 1 are used to compute the thermal conductivity of the nanoparticle-fluid mixtures made in this work. The computed results of  $\text{Al}_2\text{O}_3$ -ethylene glycol are shown in Figs. 5a and 5b, together with the measured data. From Figs. 5a and 5b, it can be seen that the measured thermal conductivity is greater than the value calculated using the effective thermal conductivity theories.



**Fig. 5** Measured thermal conductivities of  $\text{Al}_2\text{O}_3$ -ethylene glycol mixtures vs effective thermal conductivities calculated from theories: a)  $\alpha = 10$  and b)  $\alpha = \infty$ .

**Table 1** Summary of theories of effective thermal conductivity of a mixture

Investigator	Expressions <sup>a</sup>	Remarks
Maxwell <sup>15</sup>	$\frac{k_e}{k_f} = 1 + \frac{3(\alpha - 1)\phi}{(\alpha + 2) - (\alpha - 1)\phi}$	1) Equation derived from electric permeability calculation 2) Accurate to order $\phi^1$ , applicable to $\phi \ll 1$ or $ \alpha - 1  \ll 1$
Jeffrey <sup>16</sup>	$\frac{k_e}{k_f} = 1 + 3\beta\phi + \phi^2 \left( 3\beta^2 + \frac{3\beta^2}{4} + \frac{9\beta^3}{16} \frac{\alpha + 2}{2\alpha + 3} + \frac{3\beta^4}{2^6} + \dots \right)$	1) Accurate to order $\phi^2$ ; high-order terms represent pair interactions of randomly dispersed spheres
Davis <sup>17</sup>	$\frac{k_e}{k_f} = 1 + \frac{3(\alpha - 1)}{(\alpha + 2) - (\alpha - 1)\phi} [\phi + f(\alpha)\phi^2 + O(\phi^3)]$	1) Accurate to order $\phi^2$ ; high-order terms represent pair interactions of randomly dispersed spheres 2) $f(\alpha) = 2.5$ for $\alpha = 10$ ; $f(\alpha) = 0.50$ for $\alpha = \infty$
Lu and Lin <sup>18</sup>	$\frac{k_e}{k_f} = 1 + a \cdot \phi + b \cdot \phi^2$	1) Near- and far-field pair interactions are considered, applicable to nonspherical inclusions 2) For spherical particles, $a = 2.25$ , $b = 2.27$ for $\alpha = 10$ ; $a = 3.00$ , $b = 4.51$ for $\alpha = \infty$
Bonnacaze and Brady <sup>19,20</sup>	N/A	1) Numerical simulation, expressions not given 2) Near- and far-field interactions among two or more particles are considered

<sup>a</sup>Effective thermal conductivity of the mixture  $k_e$ , thermal conductivity of the fluid  $k_f$ , ratio of thermal conductivity of particle to thermal conductivity of fluid  $\alpha$ , and volume fraction of particles in fluid  $\phi$ .

In the calculation, the thermal conductivity of  $\text{Al}_2\text{O}_3$  nanoparticles is taken as  $2.5 \text{ W/m} \cdot \text{K}$  ( $\alpha = 10$ ), lower than its bulk value of  $36 \text{ W/m} \cdot \text{K}$ . No thermal conductivity data of the  $\gamma$ - $\text{Al}_2\text{O}_3$  nanoparticles are available. It is known that in the micro- and nanoscale regime the thermal conductivity is lower than that of the bulk materials. For example, it was found, through solving the Boltzmann transport equation of heat carrier in the host medium, that heat transfer surrounding a nanometer-size particle whose mean free path is on the order of its physical dimension is reduced and localized heating occurs.<sup>23</sup> The mean free path in polycrystalline  $\text{Al}_2\text{O}_3$  is estimated to be around 5 nm. Although the mean free path is smaller than the diameter of the particles, the  $\gamma$ -phase  $\text{Al}_2\text{O}_3$  particles used in this work consist of highly distorted structures. Therefore, it is expected that the mixture's thermal conductivity is reduced. On the other hand, from Fig. 5b, it can be seen that the measured thermal conductivity of the mixture is greater than the value calculated using the effective thermal conductivity theories even when the thermal conductivity of  $\text{Al}_2\text{O}_3$  is taken as infinity. Therefore, the theoretical models, which compared well with the measurements of dispersions with large size (micrometer or larger) particles, underpredict the thermal conductivity increase in nanoparticle-fluid mixtures. This suggests that all of the current models, which only account for the differences between thermal conductivity of particles and fluids, are not sufficient to explain the energy transfer processes in nanoparticle-fluid mixtures.

### C. Mechanisms of Thermal Conductivity Increase in Nanoparticle-Fluid Mixtures

In nanoparticle-fluid mixtures, other effects such as the microscopic motion of particles, particle structures, and surface properties may cause additional heat transfer in the fluids. These effects are discussed as follows.

#### 1. Microscopic Motion

Because of the small size of the particles in the fluids, additional energy transport can arise from the motions induced by stochastic (Brownian) and interparticle forces. Motions of particles cause microconvection that enhances heat transfer. In all of the effective conductivity models discussed earlier, the particles are assumed to be stationary when there is no bulk motion of the fluids, which is true when the particle is large. In nanoparticle-fluid mixtures, microscopic forces can be significant. Forces acting on a nanometer-size particle include the Van der Waals force, the electrostatic force resulting from the electric double layer at the particle surface, the stochastic force that gives rise to the Brownian motion of particles, and the hydrodynamic force. Motions of the particles and fluids are induced and affected by the collective effect of these forces. Notice that the stochastic force and the electrostatic force are significant only for small particles, whereas the Van der Waals force is high when the distance between particles is small. Therefore, there exists a relation between the effective thermal conductivity and the particle size, as observed by comparing the data obtained in this work with reported values. However, these forces have not been calculated accurately because they are strongly influenced by the chemical properties of the particle surface and the hosting fluid, the size distribution, and the configuration of the particle system. Little quantitative research has been done on the heat transfer enhancement by the microscopic motion induced by these forces.

The heat transfer enhancement due to the Brownian motion can be estimated with the known temperature of the fluid and the size of the particles. The increase of thermal conductivity due to the rotational motion of a spherical particle can be estimated as<sup>24</sup>

$$\Delta k_{e,r} = k_f \cdot \phi \cdot \left[ \frac{1.176(k_p - k_f)^2}{(k_p + 2k_f)^2} + 5 \times \left( 0.6 - 0.028 \frac{k_p - k_f}{k_p + 2k_f} \right) \right] Pe_f^{\frac{3}{2}} \quad (3)$$

where  $Pe_f = (r^2 \gamma \rho c_{p_f} / k_f)$ ,  $r$  is the radius of particle,  $\gamma$  is the velocity gradient calculated from the mean Brownian motion velocity and the average distance between particles,  $\rho$  is the base liquid density, and  $c_{p_f}$  is the specific heat of base liquid. The thermal transport caused by the translational movement of particles was given by Gupte et al.<sup>25</sup> In their study, the base liquid and particles were assumed to have identical thermal conductivity, density, and heat capacity. Their results are fitted with a fourth-order polynomial as

$$\Delta k_{e,t} = (0.0556Pe_t + 0.1649Pe_t^2 - 0.0391Pe_t^3 + 0.0034Pe_t^4)k_f \quad (4)$$

where the modified Peclet number is defined as  $Pe_t = (UL\rho c_{p_f} / K_f)\phi^{3/4}$ ,  $U$  is the velocity of the particles relative to the base liquid, and  $L = (r/\phi^{1/3}) \cdot (4\pi/3)^{1/3}$ . The total increase in thermal conductivity by the Brownian motion of particles consists of the increases due to both translational and rotational motions. However, it can be seen from Eqs. (3) and (4) that the increase in thermal conductivity is small because of the small (modified) Peclet number, meaning that heat transferred by advection of the nanoparticles is less than that transferred by diffusion. In other words, when the particles move in liquid, the temperature of the particles quickly equilibrate with that of the surrounding fluids due to the small size of the particles. Calculations based on Eqs. (3) and (4) show that up to a volume fraction of 10%, the thermal conductivity increase by the Brownian motion is less than 0.5% for the  $\text{Al}_2\text{O}_3$ -liquid mixture. Therefore, the Brownian motion does not contribute significantly to the energy transport in nanoparticle-fluid mixtures.

It is difficult to estimate the microscopic motions of particles caused by other microscopic forces and the effects of these forces on heat transfer. The surfaces of metal oxide particles are terminated by a monolayer of hydroxyl (OH) when the particles are exposed to water or water vapor. This monolayer will induce an electric double layer,<sup>26</sup> the thickness of which varies with the fluids and the chemical properties of the particle surface. For weak electrolytic solutions, a typical double-layer thickness is between 10 and 100 nm (Ref. 27). Therefore, when the particle size is in the tens of nanometers, the thickness of the double layer is comparable to the size of the particle. On the other hand, for the fluids used in this work whose particle volume fraction is a few percents, the average distance between particles is about the same as the particle size, in the tens of nanometers. For example, for 5 vol%  $\text{Al}_2\text{O}_3$ , the average distance between particles is about 33 nm. When the distance between the particles is as small as tens of nanometers, the Van der Waals force is significant. The electric double layer and the Van der Waals force could have strong electrokinetic effects on the movement of the nanoparticles and on the heat transport process.

#### 2. Chain Structure

Studies of nanoparticles by transmission electron microscopy (TEM) show that the  $\text{Al}_2\text{O}_3$  particles used in this work are spherical. However, some particles in the liquids are not separated completely. Using TEM, it is found that some particles adhere together to form a chain structure. According to Hamilton and Crosser,<sup>28</sup> heat transfer could be enhanced if the particles form chain structures because more heat is transported along those chains oriented along the direction of the heat flux. The effect of the particle size is not considered in their treatment. Assuming that an average chain consists of three particles, the thermal conductivity of particles is 10 times that of the base liquid, and there is 5 vol% particles in liquid, the thermal conductivity will increase 3% according to Hamilton and Crosser's equation.<sup>28</sup> If the thermal conductivity ratio is taken as infinity, the increase of thermal conductivity is about 7%. Therefore, it is possible that the chain structure contributes to a thermal conductivity increase in nanoparticle-fluid mixtures. However, the actual particle structures in liquids may not be preserved when the TEM measurements are taken. Therefore, the effects of particle structures are not accurately determined. Currently, there are no techniques available for characterizing the structures of nanoparticles in liquid.

#### D. Viscosity of Nanoparticle-Fluid Mixtures and Applications of Nanoparticle-Fluid Mixtures for Heat Transfer Enhancement

Because of the increased thermal conductivity of nanoparticle-fluid mixtures over the base liquids, nanoparticle-fluid mixtures can be used for heat transfer enhancement. On the other hand, the viscosity of the mixtures should also be taken into account because it is one of the parameters that determine the required pumping power of a heat transfer system.

Figure 6 shows the relative viscosity of  $\text{Al}_2\text{O}_3$ -water solutions dispersed by different techniques, that is, mechanical blending (method 1), coating particles with polymers (method 2), and filtration (method 3). These viscosity data are obtained with a precalibrated viscometer. It is seen that the solutions dispersed by methods 2 and 3 have lower viscosity, indicating that the particles are better dispersed. (It is a common practice to determine whether particles are well dispersed based on whether or not the viscosity value is minimized.<sup>29</sup>) The  $\text{Al}_2\text{O}_3$ -water mixture shows a viscosity increase between 20 and 30% for 3 vol%  $\text{Al}_2\text{O}_3$  solutions compared to that of water alone. On the other hand, the viscosity of  $\text{Al}_2\text{O}_3$ -water used by Pak and Cho<sup>11</sup> was three times higher than that of water. This large discrepancy could be due to differences in the dispersion techniques and differences in the size of the particles.

The viscosity of the  $\text{Al}_2\text{O}_3$ -ethylene glycol solution is shown in Fig. 7. Compared with the  $\text{Al}_2\text{O}_3$ -water solution, the  $\text{Al}_2\text{O}_3$ -ethylene glycol solution has a similar viscosity increase but a higher thermal conductivity increase.

For laminar flow in a circular tube, the convection heat transfer coefficient is proportional to the thermal conductivity of the fluid, whereas the pressure drop is proportional to viscosity. For turbulence flow in a circular tube, the pressure drop is proportional to  $\mu^{1/5}$ , whereas the convection heat transfer coefficient is proportional to  $(k_f^{2/3}/\mu^{0.467})$  according to the Colburn's equation (see Ref. 13). Using the measured thermal conductivity and viscosity data, the increase in pressure drop is found to be about the same as the increase in heat transfer for all of the fluid-particle mixtures studied in this work. This estimation is based on the assumption that there are no other heat transfer mechanisms in the flow of the fluids

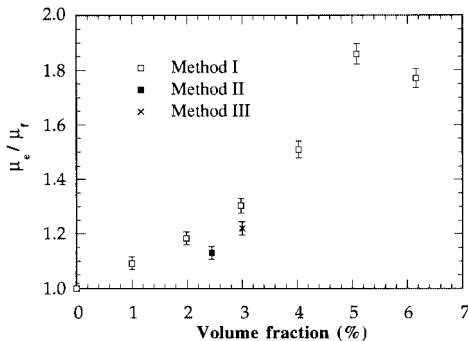


Fig. 6 Relative viscosity of  $\text{Al}_2\text{O}_3$ -water mixtures dispersed by three different methods.

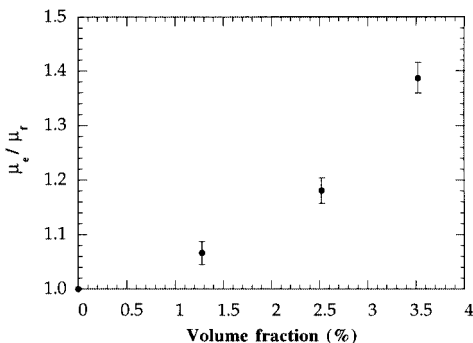


Fig. 7 Relative viscosity of  $\text{Al}_2\text{O}_3$ -ethylene glycol mixtures.

with nanoparticles. With this assumption, the desirable heat transfer increase is offset by the undesirable increase in pressure drop. However, when fluids with nanoparticles are flowing in a channel, motions of particles also enhance heat transfer due to the decreased thermal boundary thickness, enhancement of turbulence, and/or heat conduction between nanoparticles and the wall as was found in the studies of gas-particle flow. Therefore, more studies are needed on convection heat transfer in fluids with nanoparticles to justify the use of them as a heat transfer enhancement medium.

#### V. Conclusions

The effective thermal conductivities of fluids with  $\text{Al}_2\text{O}_3$  and CuO nanoparticles dispersed in water, vacuum pump fluid, engine oil, and ethylene glycol are measured. The experimental results show that the thermal conductivities of nanoparticle-fluid mixtures increase relative to those of the base fluids.

A comparison between the present experimental data and those of other investigators shows a possible relation between the thermal conductivity increase and the particle size: The thermal conductivity of nanoparticle-fluid mixtures increases with decreasing the particle size. The thermal conductivity increase also depends on the dispersion technique.

Using existing models for computing the effective thermal conductivity of a mixture, it is found that thermal conductivities computed by theoretical models are much lower than the measured data, indicating the deficiencies of the existing models in describing heat transfer at the nanometer scale in fluids. It appears that the thermal conductivity of nanoparticle fluid mixtures is dependent on the microscopic motion and the particle structure. Any new models of thermal conductivity of liquids suspended with nanometer-size particles should include the microscopic motion and structure-dependent behavior that are closely related to the size and surface properties of the particles. To use nanoparticle-fluid mixtures as a heat transfer enhancement medium, more studies on heat transfer in the fluid flow are needed.

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