NANOFLUIDS CAN TAKE THE HEAT

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ABSTRACT

Copper nanoparticles and carbon nanotubes have been found to enhance the thermal conductivity of base fluids dramatically. Adding ~0.3 vol.% of 10-nm copper nanoparticles to ethylene glycol increased its thermal conductivity up to 40%. Nanotubes yield by far the highest thermal conductivity enhancement ever achieved in a liquid: a 150% increase in the conductivity of oil at ~1 vol.% of 25-nm nanotubes. More interestingly, the thermal conductivity enhancement with the nanotubes is an order of magnitude higher than predicted by existing theories. This discovery clearly suggests that conventional heat conduction models for solid/liquid suspensions are inadequate. Several mechanisms that could be responsible for thermal transport in nanofluids have been proposed. However, the mysteries of nanoparticles in fluids remain unsolved, presenting new opportunities and challenges for scientists and engineers. Nanofluid research could lead to a major breakthrough in solid/liquid composites for numerous engineering applications, such as coolant for automobiles, air conditioning, and supercomputers.

INTRODUCTION

There is a great need for more efficient heat transfer fluids in many industries, from transportation to energy supply to electronics and photonics. The coolants, lubricants, oils, and other heat transfer fluids used in today's thermal management systems have inherently poor heat transfer properties. And conventional working fluids that contain millimeter- or micrometer-sized particles are not applicable to the newly emerging "miniaturized" technologies because they can clog microchannels.

Modern nanotechnology allows one to process and produce materials with average crystallite sizes <50 nm. Recognizing an opportunity to apply this emerging nanotechnology to established thermal energy engineering, Argonne National Laboratory (ANL) has developed "nanofluids" [1]. Nanofluids are a new, innovative class of heat transfer fluids created by dispersing solid particles smaller than 40 nm in diameter (less than one-thousandth the diameter of a human hair) in traditional heat transfer fluids such as water, engine oil, and ethylene glycol. Solid particles are added because they conduct heat much better than liquid. In addition, compared with microparticles, nanoparticles stay suspended much longer and possess much higher surface area (1,000 times). The latter enhances the heat conduction of nanofluids since heat transfer occurs on the surface of the fluid. Therefore, by exploiting the unique properties of nanoparticles, we are able to create nanofluids with an unprecedented combination of the two features most highly desired for heat transfer systems: extreme stability and ultra-high thermal conductivity.

The enhanced thermal conductivity of nanofluids is not merely of academic interest. There is now great industrial interest in nanofluids. Benefits of nanofluids include dramatically improved heat transfer, smaller heat exchangers, reduced inventories of heat transfer fluids, and reduced energy consumption for pumping heat transfer fluids [1-3]. In vehicles, for example, smaller components result in better gas mileage, fuel savings to consumers, and a cleaner environment due to fewer emissions.

Another very important advantage of nanofluids is related to particle size. The use of conventional particles in heat transfer fluids in practical devices is greatly limited by the tendency of such particles to settle rapidly and to clog mini- and micro-channels. However, nanoparticles appear to be ideally suited for applications in which fluids flow through small passages, because the nanoparticles are stable and small enough not to clog flow passages. These desirable properties have led to the possibility of using nanoparticles in microchannels for advanced cooling applications [4].

PRODUCTION AND CHARACTERIZATION OF NANOFLUIDS

ANL developed two methods for producing nanofluids: the one-step direct evaporation method, which involves evaporating the particles directly into base fluids, and the two-step "Kool-Aid" method, which involves preparing nanoparticles and then dispersing them into the base fluids. In either case, a well-mixed and uniformly dispersed nanofluid is needed for successful reproduction of properties and interpretation of experimental data.

Very stable and highly conductive copper nanofluids were produced by the single-step method [5]. As shown in Fig. 1, this method resulted in very small (an average diameter of less than 10 nm) particles. Loadings of up to approximately 0.5 vol.% of nanocrystalline copper particles were dispersed into ethylene glycol with little agglomeration. Particle loadings were estimated by weighing the resistive evaporation source before and after the nanofluid preparation. For some nanofluids, a small amount of thioglycolic acid (< 1 vol.%) was added to further improve the particle dispersion behavior.

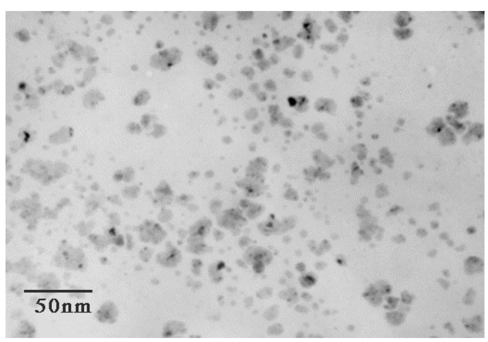

Fig. 1. Bright-field transmission electron micrograph of Cu nanoparticles produced by direct evaporation into ethylene glycol. Very little agglomeration occurs with this processing method. (Reprinted from Applied Physics Letters, Vol. 78, Eastman et al., pp. 718-720, 2001, with permission from American Institute of Physics.)

Recently, nanotube-in-oil suspensions were produced by the two-step method [6]: first, multiwalled carbon nanotubes (MWNTs) were generated in a chemical vapor deposition reactor, with xylene as the primary carbon source and ferrocene as an iron catalyst [7]. The metallic MWNTs, which were typically straight in their as-grown form (Fig. 2), had a mean diameter of ~25 nm and a length of ~50 μm (for an average aspect ratio of ~2000) and contained an average of 30 annular layers. Second, the MWNTs were dispersed into a synthetic poly (α - olefin) oil. Well-dispersed and stable suspensions with loadings of up to 1 vol.% nanotubes were produced and tested.

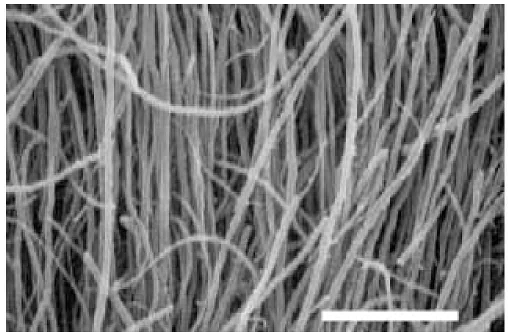

Fig. 2. Scanning electron photomicrograph of multiwall nanotubes used in this study. Conventional gold sputtering technique was employed to coat sample. Photo taken by high-resolution HITACHI S-2700 scanning electron microscope. Scale bar is 800 nm. (Reprinted from Applied Physics Letters, Vol. 79, Choi et al., pp. 2252-2254, 2001, with permission from American Institute of Physics.)

THERMAL CONDUCTIVITY OF NANOFLUIDS

The thermal conductivity of nanofluids that contain copper nanoparticles or carbon nanotubes was measured as a function of nanoparticle volume fraction at room temperature by the transient hot-wire (THW) method [5-6]. The THW method is one of the most accurate for determining thermal conductivities of materials [8-12]. The major advantage of this method lies in its almost complete elimination of the effects of natural convection, whose unwanted presence creates problems for measurements made with a steady-state apparatus. In addition, the method is very fast relative to steady-state techniques.

We designed and fabricated a THW system with a platinum wire suspended symmetrically in a liquid in a vertical cylindrical container. The Pt wire was coated with a thin electrical insulation layer to avoid problems associated with the measurement of electrically conducting fluids [9]. Calibration experiments were performed for ethylene glycol in the temperature range of 290 K to 310 K and at atmospheric pressure. Literature values [13] were reproduced with an error of <1.5%.

Figure 3 shows the measured thermal conductivity of Cu-containing ethylene glycol nanofluids as a function of nanoparticle volume fraction. The change in thermal conductivity of the nanofluid is plotted relative to that of its base fluid (k_e is the effective thermal conductivity of nanofluids, and k_f the thermal conductivity of the base fluid). Figure 3 also shows the thermal conductivity enhancement of ethylene glycol + Al_2O_3 and ethylene glycol + CuO [2]. Clearly, nanofluids that contain metallic Cu nanoparticles exhibit a much higher thermal conductivity ratio (up to 1.4 times at particle loadings well below 1 vol.%) than those that contain oxides. Also, nanofluids containing thioglycolic acid as a stabilizing agent show improved behavior compared to non-acid-containing nanofluids, while fluids containing thioglycolic acid, but no particles, had no improvement in thermal conductivity. Interestingly, fresh copper nanofluids tested within two days of preparation exhibited slightly higher conductivities than fluids that were stored up to two months prior to measurement.

Figure 4 shows the measured thermal conductivity of the nanotube-in-oil suspensions as a function of the volume fraction of nanotubes. Clearly, nanotubes yield an anomalously large increase in thermal conductivity (up to a 150% increase in conductivity of oil at approximately 1 vol.% nanotubes), which is by far the highest thermal conductivity enhancement ever achieved in a liquid. More surprisingly, the observed increase in thermal conductivity of nanotube nanofluids is an order of magnitude higher than predicted from existing theories [6]. In the model predictions, the thermal conductivity of the nanotube is taken as 3000 W/m•K [14], and that of the oil as 0.1448 W/m•K.

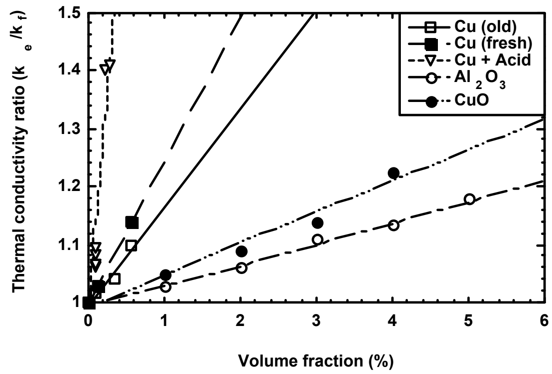

Fig. 3. Thermal conductivity enhancement of copper, copper oxide, and alumina particles in ethylene glycol. Significantly greater enhancements are seen for nanofluids consisting of <10-nm diameter Cu nanoparticles than for either CuO or Al_2O_3 nanoparticles of average diameter 35 nm. (Reprinted from Applied Physics Letters, Vol. 78, Eastman et al., pp. 718-720, 2001, with permission from American Institute of Physics.)

In Fig. 4, we see another anomaly. The measured thermal conductivity is nonlinear with nanotube loadings, while all theoretical predictions clearly show a linear relationship. This nonlinear behavior is not expected in conventional fluid suspensions of micrometer-sized particles at such low concentrations. Our experiments imply the existence of nanotube/nanotube interactions, even at extremely low nanotube volume fractions, possibly because of the astronomical number of nanotubes in the liquid and the extremely high aspect ratio (~2000) of the carbon nanotubes.

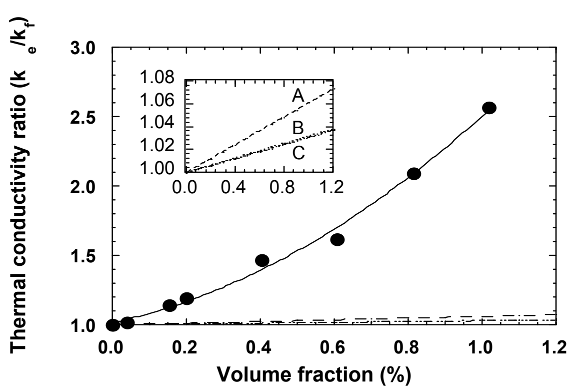

Fig. 4. Measured and predicted thermal conductivity enhancement for nanofluids. Dispersion of a very small amount of nanotubes produces a remarkable change in effective thermal conductivity of the base fluid, with the thermal conductivity ratio exceeding 2.5 at 1 vol.% nanotubes. Comparison of measured data for nanotube suspensions (solid circles) and those predicted by theories (dotted lines) shows that the measured values are one order of magnitude greater than predictions at 1 vol.% nanotubes. Because all calculated values are almost identical at the low volume fractions, some of the calculated values are reproduced on an expanded scale in the inset, where line A = Hamilton-Crosser [15]; line B = Bonnecaze & Brady [16, 17]; line C = Maxwell [18]. (Reprinted from Applied Physics Letters, Vol. 79, Choi et al., pp. 2252-2254, 2001, with permission from American Institute of Physics.)

POTENTIAL MECHANISMS

We have used various theoretical models [15-22] to compute the thermal conductivities of fluid/particle mixtures. However, our efforts to explain the observed anomalous thermal behavior have been unsuccessful. According to the models currently used for traditional solid/liquid suspensions, the effective thermal conductivity of liquid/particle suspensions depends only on the volume fraction and shape of the suspended particles. All the conventional models do not account for particle size, which may not be a key parameter for fluids with large particles. In fact, all of the previous theories of the thermal conductivity of solid/liquid systems were developed for fluids with particles that are three to six orders of magnitude larger than nanoparticles. Only recently have nanoparticles of 50 nm or less become available to investigators. Experiments with nanofluids have shown that all existing theories, models, and correlations for thermal conductivity are very limited and often contradictory when applied to fluids that contain nanoparticles. Thus, our discovery clearly suggests that conventional heat conduction models for solid/liquid suspensions are inadequate.

To our knowledge, no theoretical studies have been conducted on the thermal conductivity of nanofluids. Thus, in parallel with the experimental studies, we conducted theoretical studies as a first step to explaining the thermal conductivity of nanofluids. We used simple physical arguments to place upper limits on the possible effects that various mechanisms could have on enhancing thermal transport and molecular dynamics simulations to illustrate how molecular-level simulation is capable of shedding light on heat transport in nanofluids. The four possible mechanisms of this anomalous increase include Brownian motion of the particles, molecular-level layering of the liquid at the liquid/particle interface, the nature of heat transport in the nanoparticles, and the effects of nanoparticle clustering [23]. Among the four, the key factors in understanding thermal properties of nanofluids are the ballistic, rather than diffusive, nature of heat transport in the nanoparticles and clustering effects that provide paths for rapid heat transport.

The effect of clustering is illustrated in Fig. 5, which plots the excess thermal conductivity enhancement κ (the ratio of measured thermal conductivity increase divided by the increase predicted by the Hamilton-Crosser theory [15]), originating from the increased effective volume of highly conducting clusters, as a function of the packing fraction of the cluster ϕ (ratio of the volume of the solid particles in the cluster to the total volume of the cluster). With decreasing packing fraction, the effective volume of the cluster increases, thus enhancing thermal conductivity. Even for a cluster of closely packed spherical particles, ≈25% volume of the cluster consists of liquid filling the space between particles. This condition increases the effective volume of a highly conductive region by ≈30% with respect to a dispersed nanoparticle system. For more loosely packed clusters the effective volume increase will be even larger.

A further dramatic increase of κ can take place if the particles do not need to be in physical contact, but just within a specific distance, allowing rapid heat flow between them. Such “liquid-mediated” clusters exhibit a very low packing fraction and thus a very large effective volume and, in principle, are capable of explaining the unusually large experimentally observed enhancements of thermal conductivity. Note, however, that clustering may exert a negative effect on heat transfer enhancement, particularly at low volume fraction, by settling small particles out of the liquid and creating large regions of "particle free" liquid with high thermal resistance.

To elucidate the nature of heat transport in the nanoparticle, we compared the autocorrelation functions of the heat flux associated with the solid J_{Qs} and liquid J_{Ql} parts of the system ($J_Q = J_{Qs} + J_{Ql}$). Both autocorrelation functions are plotted in Fig. 6. The function J_{Ql} decays monotonically to zero and is very similar to the autocorrelation function that characterizes a pure liquid. By contrast, J_{Qs} decays to zero in an oscillatory manner and exhibits negative values. Such negative values are signatures of “back scattering,” indicating that phonons carrying heat energy are reflected by the solid/liquid interfaces. Such reflection is not surprising, considering that the solid is much stiffer than the liquid. We verified that the period of oscillations corresponds to the time needed for a phonon to travel across the particle, and that it scales with increasing particle size.

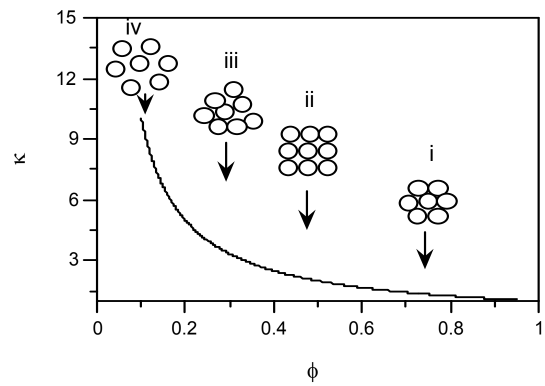

Fig. 5. Excess thermal conductivity enhancement κ due to increased effective volume ϕ of highly conducting clusters. Schematics above curve indicate (from right to left) (i) closely packed face-centered-cubic arrangement of particles, (ii) simple cubic arrangement, (iii) loosely packed irregular structure of particles in physical contact, and (iv) clusters of particles separated by liquid layers thin enough to allow for rapid heat flow among particles. (Reprinted from Int. J. Heat Mass Trans., Vol. 45, Keblinski et al., pp. 855-863, 2002, with permission from Elsevier Science)

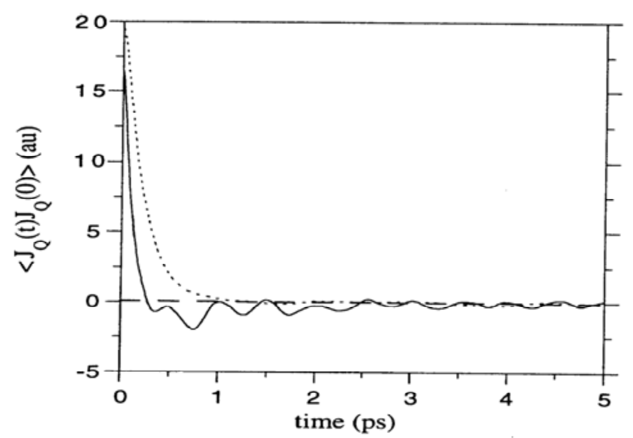

Fig. 6. Heat current autocorrelation functions for liquid (dashed line) and particle (solid line). Curves indicate monotonic decay of correlations in liquid and oscillatory decay in solid, a signature of ballistic phonons moving back and forth inside the particle. (Reprinted from Int. J. Heat Mass Trans., Vol. 45, Keblinski et al., pp. 855-863, 2002, with permission from Elsevier Science)

The above results clearly demonstrate that inside solid particles, heat moves in a ballistic manner that involves multiple scattering from the solid/liquid interface. Also, these results demonstrate that particle/liquid interfaces play a key role in translating fast thermal transport in particles into high overall conductivity of the nanofluid. The main characteristic of the interface from this perspective is the transmission coefficient, i.e., how much heat is able to go through the solid/liquid interface rather than reflect back into the particle, thereby not contributing to macroscopic heat transport.

CURRENT RESEARCH DIRECTIONS

At present, we still do not have a fundamental and quantitative understanding of the thermal conductivity mechanisms in nanofluids. Thus, our current research is focused on a theoretical and experimental study to answer the question, “How does particle size affect thermal conductivity?” We are working to build a structural model that can help explain the thermal conductivity of nanofluids. A key parameter in this new model will be the particle size, which is absent from the old models. One of the challenges is to develop a tool to measure the thermal conductance between two nanoparticles that are suspended in liquid less than 50 nm apart. This new tool is needed to better understand the physics responsible for the anomalous increase in conductivity and to validate a new model. In addition to particle size, particle motion induced by stochastic, interparticle, or other forces could be significant at the nanometer scale. Such motions may contribute significantly to energy transport at the nanometer scale. Another major task is analyzing the microscopic motions in nanofluids and understanding their contribution to energy transport.

We have presented results of molecular dynamics simulations for a single-model system; however, this approach can be used to explore various model systems. For example, we are simulating particles with different sizes (up to 10 nm in diameter, which is at the lower end possible with present experimental systems) and exploring the effects of clustering in multiparticle systems. The results of such simulations will enable us to address the role of particle size and interparticle separation on heat flow.

Another interesting fundamental issue related to nanofluids is that, while the thermal conductivity of nanoparticles significantly decreases with decreasing nanoparticle size [24, 25] relative to that of the bulk materials used to produce nanoparticles, the thermal conductivity of nanofluids increases with decreasing particle size. Therefore, an investigation is being conducted to study the thermal conductivity of nanometer-size copper particles. The overall thermal conductivity of copper pellets made of such particles is measured by the photoacoustic method [26, 27].

CONCLUDING REMARKS

We produced nanofluids containing copper nanoparticles by the one-step method and carbon nanotubes by the two-step method, and showed that these solids enhance the thermal conductivity of the base fluids dramatically. For example, adding only 0.3 vol.% of 10-nm copper nanoparticles to ethylene glycol increased its thermal conductivity up to 40%. Further, nanotubes have yielded by far the highest thermal conductivity enhancement ever achieved in a liquid: a 150% increase in conductivity of oil at ~1 vol.% of 25-nm nanotubes. More interestingly, nanofluids can conduct heat one order of magnitude faster than predicted possible. Several possible mechanisms of this anomalous increase have been proposed and are under investigation. A better understanding of the mechanisms behind the thermal-conductivity enhancement will likely lead to recommendations for nanofluid design and engineering for industrial applications. On the basis of the promising results to date, nanofluid research could lead to a major breakthrough in solid/liquid composites for numerous engineering applications, such as coolant for automobiles, air conditioning, and supercomputers.

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