NANOFLUID TECHNOLOGY: CURRENT STATUS AND FUTURE RESEARCH

Stephen U.-S. Choi
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

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ABSTRACT (in Korean)

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ABSTRACT

Downscaling or miniaturization has been a recent major trend in modern science and technology. Engineers now fabricate microscale devices such as microchannel heat exchangers, and micropumps that are the size of dust specks. Further major advances would be obtained if the coolant flowing in the microchannels were to contain nanoscale particles to enhance heat transfer. Nanofluid technology will thus be an emerging and exciting technology of the 21st century.

This paper gives a brief history of the Advanced Fluids Program at Argonne National Laboratory (ANL), discusses the concept of nanofluids, and provides an overview of the R&D program at ANL on the production, property characterization, and performance of nanofluids. It also describes examples of potential applications and benefits of nanofluids. Finally, future research on the fundamentals and applications of nanofluids is addressed.

1 INTRODUCTION

Since Nobel prize winner Richard Feynman presented the concept of micromachines in 1959, miniaturization has been a major trend in modern science and technology. Almost 40 years later, another Nobel prize winner, H. Rohrer, presented the chances and challenges of the "nano-age" (Rohrer, 1996). The steady miniaturization trend has dropped from the millimeter scale of the early 1950s to the present-day atomic scale (Sohn, 1998). The concept and development of nanofluids is directly related to trends in miniaturization and nanotechnology. The pioneering efforts at Argonne National Laboratory (ANL) are keyed to potential commercial applications of nanofluids in many diverse industries.

This paper provides an overview of ANL's nanofluid technology. First of all, we will discuss the miniaturization trend and nanotechnology because they are related to the development of nanofluids technology. After briefly describing the history of ANL's Advanced Fluids Program to show how the concept of nanofluids has been developed, we will discuss the concept of nanofluids, the technology for producing nanoparticles and nanofluids, and thermal conductivity and heat transfer measurements of nanofluids with oxide nanophase materials. We will also explore the potential benefits of nanofluids to show that ultra-high-performance nanofluids can have major implications for many industries. It is shown that one of the benefits of nanofluids will be dramatic reductions in heat exchanger pumping power. Finally, we will discuss the fundamental issues related to the development of nanofluids.

2 MINIATURIZATION AND NANOTECHNOLOGY

Just as downsizing is a fashion in the world of business, downscaling is a clear trend in the world of science and technology. As the age of "bigger is better" gives way to the age of "smaller is better," microelectromechanical systems (MEMS) technology and nanotechnology are rapidly emerging as the new revolution in miniaturization. One feature of these rapidly emerging technologies is that they are strongly interdisciplinary. In the coming micro- and nano-age, the miniaturization technology with unforeseen applications is expected to revolutionize many industries.

A variety of micro-scale products are already available, or soon will be. Miniaturized sensors, actuators, motors, heat exchangers, pumps, heat pumps, valves, heat pipes, fuel cells, instruments, medical devices, robots, and airplanes are just a few of the almost endless variety of micro products in the market or poised to move from the laboratory to the marketplace. These micro components will also be integrated to build complex MEMS and other systems.

Miniature heat exchangers have numerous attributes, including high thermal effectiveness, high heat transfer surface-to-volume ratio, small size, low weight, low fluid inventory, and design flexibility. Because their microchannel systems are extremely compact and lightweight compared to conventional systems, materials and manufacturing costs could be lowered, an attractive advantage that would draw the interest of many manufacturing firms. For example, the electronics industry has applications in cooling advanced electronic packages; for the automotive industry, the weight difference between conventional and microchannel systems (such as in air

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conditioners) could lead to significant gains in fuel economy; in the HVAC industry, refrigeration and air conditioning equipment volumes could be reduced and this would save space in buildings; and in chemical and petroleum plants, plant size could be reduced through "process intensification." The trend toward miniaturization is also apparent in the U.S. Space Program, which is developing ultralight spacecraft using MEMS, and in energy industries that are designing microcogeneration systems (1-10 kW$_e$) using micro gas turbines and micro engines.

From virtual obscurity about a decade ago, nanoscience and nanotechnology have entered the limelight (Rohrer, 1996). Recent reviews of research programs on nanotechnology in the U. S., China, Europe, and Japan show that nanotechnology will be an emerging and exciting technology of the 21st century and that universities, national laboratories, small businesses, and large multinational companies have established nanotechnology research groups or interdisciplinary centers that focus on nanotechnology (Roco, 1998; Li, 1998; Fissan and Schoonman, 1998; Hayashi and Oda, 1998). It is estimated that nanotechnology is at a similar level of development as computer/information technology was in the 1950s (Roco, 1998). Nanomaterials have unique mechanical, optical, electrical, magnetic, and thermal properties.

After nanotechnology will come a technology for building up systems and structures from atoms and molecules via nanoparticles, nanotubes, and nanolayers. One can imagine that once scientists and engineers reach the atomic and molecular scale, they will be able to build systems and structures by using bottom-up methods, starting from atoms and molecules, rather than current top-down methods such as micromachining, lithography, and etching.

3 A BRIEF HISTORY OF THE ADVANCED FLUIDS PROGRAM AT ARGONNE

The advanced fluids program at ANL has encompassed a wide range (meters to nanometers) of size regimes. It is interesting to see how a wide research road has become narrow, starting with large-scale and descending through mini- and micro-scales to nano-scale in this program.

Large-Scale Experiments

In 1985, ANL started a long-term research program to develop advanced energy transmission fluids. The Buildings and Community Systems staff in the U.S. Department of Energy (DOE) were very generous in providing sufficient funding for this program. Early efforts focused on the development of advanced energy transmission fluids for use in district heating and cooling (DHC) systems. These systems are characterized by long distribution pipes of large diameter that convey pumped energy transmission fluids between the source and sink heat exchangers. These systems operate with small temperature differences, and therefore large volumes of fluids must be pumped to satisfy load demands. The Advanced Fluids Program for DHC applications included friction-reducing additives (FRAs) and phase-change materials (Choi et al., 1992a, 1992b; Choi and Tran, 1991). Therefore, advanced energy transmission fluids for DHC systems consisted of the appropriate friction-reducing additives, phase-change particles, and a carrier liquid.

Friction-reducing additives (FRAs) of three types—a linear polymer, a surfactant, and a nylon fiber—have been tested in a large-scale DHC system simulator with a pipe diameter of 0.15 m and a length of 21.34 m. Large-scale tests have shown that the linear polymer (Separan) degrades completely. A problem encountered with 1-mm nylon fiber slurry was the plugging of a 16-mm feed line and a 12.7-mm globe valve when pumping nylon fiber suspensions from the preparation tank to the 14-m^3 simulator tank. Most surprisingly, a centrifugal pump driven by a 50-hp motor failed to rotate because the 1-mm nylon fibers plugged the clearance between the balance ring and the housing. The fibers that accumulated in the phase clearance path formed thin sheets. This finding clearly demonstrated that nylon fibers were not practical for DHC applications.

Fortunately, large-scale testing with a 2306 wt. ppm surfactant (Kemamine EX-300) solution with 2000 wt. ppm sodium salicylate has shown that this surfactant can achieve a pressure drop reduction of up to 80% and has a long lifetime in large pipes. Benefits from the successful application of surfactant FRAs could be substantial: up-front capital investment could be reduced by at least 30% in new systems. Existing systems that run on advanced energy transmission fluids with surfactant FRAs could reduce pumping power by as much as 80%, resulting in a substantial saving in operating costs. However, when this surfactant was almost ready for commercialization, we learned that it is toxic to fish and therefore not environmentally friendly. Consequently, all subsequent tests involving linear polymers, surfactants, and nylon fibers were stopped. However, that was not the end of the story of advanced fluids research at ANL.

Realizing that large-scale experiments are too costly, we had to find an exit from large-scale tests. The author learned that mirror cooling was an important issue at ANL's new Advanced Photon Source (APS). His proposal was funded by the APS Laboratory Directed Research and Development (LDRD) program. This project represented a dramatic downscaling from 0.15-m pipe to 50 μm channels. However, he did not stop in this microworld, but continued his downscaling journey until his research culminated in the invention of nanofluids.

Miniscale Heat Transfer

A shell-and-tube heat exchanger has a typical channel size of about 25 mm, while minichannel heat exchangers have channel dimensions of less than 10 mm. ANL's miniscale heat transfer projects involve phase-change heat transfer in compact heat exchangers and the application of compact heat exchangers in the process industries, with funding by DOE and with industry cost-sharing. In this way, ANL has established itself in the area of multiphase flow and heat transfer in minichannels.

For several years, ANL's experts in two-phase heat transfer have been working in the area of evaporation and condensation of refrigerants in circular or noncircular minichannels of different sizes, with the objective of developing design correlations and predictive methods. The evaporator studies have used minichannels with hydraulic diameters in the 2-3 mm range. Our condensation studies with a leading U.S. manufacturer of heat exchangers for the transportation industry have focused on multipassage tubes with hydraulic diameters as small as 0.5 mm

(approaching the upper end of the microchannel range). This work thus represents a successful downscaling of evaporators and condensers by approximately one order of magnitude (Tran et al., 1996; Wambsganss et al., 1991, 1993).

Microscale Heat Transfer

While miniscale heat exchangers are small and effective, microscale heat exchangers have the potential to further reduce the size and effectiveness of various heat exchange devices. As microelectronics technology advances through ever-increasing levels of speed and performance, the demands on cooling of advanced electronic packages such as multichip modules have also increased. These demands have given rise to major new efforts for developing microchannel cooling technology (Tuckerman and Peace, 1981). The present-day manufacturing and application of microchannel structures with characteristic dimensions of less than 0.1 mm represents an engineering breakthrough.

Argonne's APS is a user facility for synchrotron radiation research. The first optical elements of the APS beamlines absorb a tremendous amount of energy that is rapidly transformed to heat as they reflect the beam. Cooling these high-heat-load X-ray optical elements proved to be a formidable task that could not be handled by conventional cooling technologies, and thus a new and innovative cooling method was needed. In 1991, the author developed an ANL LDRD program to design and analyze a microchannel heat exchanger that uses liquid nitrogen as the cooling fluid. The work by Choi et al. (1992c) on microchannel liquid nitrogen cooling of high-heat-load silicon mirrors represents a milestone in the area of microscale forced convection heat transfer (Duncan and Peterson, 1994). This LDRD project was crucial in positioning the author for bridging microtechnology with nanotechnology, as described in the next section.

Nanoscale Heat Transfer

When the author worked on microchannel liquid nitrogen cooling, he noted its limit that the pressure drop in the microchannel heat exchanger increases significantly as the diameter of the flow passage decreases and that a cryogenic system is needed for liquid nitrogen cooling. In a microchannel liquid nitrogen heat exchanger, the heat transfer would be excellent but at the cost of high pumping power and an expensive cryogenic system. Furthermore, continuing cooling demands from future X-ray source intensities at the APS have driven the author to think of a new heat transfer enhancement approach. He wanted to develop a new heat transfer fluid concept that enables heat transfer enhancement without a large pumping power increase and without cryogenic coolants. So he focused on the thermal conductivity of the fluid itself rather than on channel size.

Although Maxwell's idea of using metallic particles to enhance the thermal conductivity of fluids is well known (Maxwell, 1873), the author realized—through his experience with nylon fiber suspensions—that conventional mini- or micrometer-sized particles cannot be used in microchannel flow passages. Therefore, he focused on a smaller world and visualized the concept of nanofluids as a way to link heat transfer fluids to the nanoparticles that have become available in recent years. This opened up the possibility of using nanoparticles in microchannels

for many envisioned high-heat-load applications. A microchannel heat exchanger with nanofluids would make a dramatic breakthrough in the development of advanced cooling technology because of a desirable combination of both large heat transfer area and high thermal conductivity (Lee and Choi, 1996).

While reading several articles on nanophase materials, the author wondered what would happen if nanoparticles could be dispersed into a heat transfer fluid. In this way, he conceived the concept of nanofluids for the development of industrial heat transfer fluids with high thermal conductivities. Specifically, the author first thought of validating the idea when he read an article in the ANL publication *logos* on nanocrystalline materials (Siegel and Eastman, 1993) and realized that ANL's Materials Science Division (MSD) has a unique capability to produce nanophase materials. DOE's Basic Energy Sciences office has funded MSD to work on the synthesis, microstructural characterization, and properties of nanophase materials, although all of that work was focused on producing nanoparticles and consolidating them to make solids and then characterizing the novel properties of these solid bulk nanophase materials.

When the author received an ANL call for LDRD proposals in May 1993, he wrote a proposal and submitted it to an annual competition within the lab for start-up funding. This proposal was not funded, however, nor was a second proposal developed with MSD's J. A. Eastman. A third proposal, in 1994, was successful. This project was funded for three years and ended in 1997. Since then, we have received additional funding from DOE to work with several companies on issues related to commercialization of nanofluids. The author and J. A. Eastman continue to collaborate on the development and hopeful eventual commercialization of nanofluids.

During the first three years of this work, we focused on (1) developing a theoretical analysis of the effective thermal conductivity of the copper/water system, taking into account different particle shapes; (2) producing nanofluids by two techniques: the single-step direct evaporation method, in which the particles are evaporated directly into base fluids and the two-step method which is first to prepare nanoparticles by the gas-condensation technique and then dispersed into the base fluids; (3) characterizing the dispersion behavior of these powders into water and ethylene glycol; (4) fabricating a new transient hot wire cell for measurement of effective thermal conductivities of nanofluids; (5) measuring the effective thermal conductivities of nanofluids; and (6) measuring the convection heat transfer coefficients of nanofluids.

In addition to our work, investigators in Japan and Germany have published articles that describe fluids resembling those developed at ANL. Masuda et al. worked on the thermal conductivity and viscosity of suspensions of Al_2O_3, SiO_2, and TiO_2 ultrafine particles and published a paper written in Japanese (Masuda et al., 1993). However, it should be noted that ANL developed the concept of nanofluids independently of the Japanese work.

While there are similarities between the Japanese work and our own, there are also several important distinctions. For example, the Japanese investigators added an acid (HCl) or base (NaOH) to produce suspensions of oxide particles because their oxide particles did not form stable suspensions in fluids. Because of these dispersants, the suspensions are not practical for commercial applications. However, we were able to make stable nanofluids with no dispersants

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at all. We discovered that our oxide nanoparticles have excellent dispersion properties and form suspensions that are stable for weeks or months. This unique feature of ANL's nanofluids is the principal distinction between the Japanese and ANL work.

In 1993, Arnold Grimm, an employee of R.-S. Automatis in Mannheim, Germany obtained a patent related to improved thermal conductivity of a fluid containing dispersed solid particles (Grimm, 1993). He dispersed Al particles measuring 80 nm to 1 μm into a fluid. He claimed a 100% increase in the thermal conductivity of the fluid for loadings of 0.5-10 vol.%. The serious problem with these suspensions was rapid settling of the Al particles, presumably because in his study the particle size was much larger than in Argonne's nanofluids work.

4 THE CONCEPT OF NANOFLUIDS

In the development of energy-efficient heat transfer equipment, the thermal conductivity of the heat transfer fluid plays a vital role. However, traditional heat transfer fluids such as water, oil, and ethylene glycol mixtures, are inherently poor heat transfer fluids. With increasing global competition, industries have a strong need to develop advanced heat transfer fluids with significantly higher thermal conductivities than are presently available.

Despite considerable previous research and development efforts on heat transfer enhancement, major improvements in cooling capabilities have been constrained because of the low thermal conductivity of conventional heat transfer fluids. However, it is well known that at room temperature, metals in solid form have orders-of-magnitude higher thermal conductivities than those of fluids (Touloukian et al., 1970). For example, the thermal conductivity of copper at room temperature is about 700 times greater than that of water and about 3000 times greater than that of engine oil, as shown in Fig. 1. The thermal conductivity of metallic liquids is much greater than that of nonmetallic liquids. Therefore, the thermal conductivities of fluids that contain suspended solid metallic particles could be expected to be significantly higher than those of conventional heat transfer fluids. In fact, numerous theoretical and experimental studies of the effective thermal conductivity of dispersions that contain solid particles have been conducted since Maxwell's theoretical work was published more than 100 years ago (Maxwell, 1873). However, all of the studies on thermal conductivity of suspensions have been confined to millimeter- or micrometer-sized particles. The major problem with suspensions containing millimeter- or micrometer-sized particles is the rapid settling of these particles. Furthermore, such particles are too large for micro systems.

Modern nanotechnology provides great opportunities to process and produce materials with average crystallite sizes below 50 nm. Recognizing an opportunity to apply this emerging nanotechnology to established thermal energy engineering, the author proposed in 1993 that nanometer-sized metallic particles could be suspended in industrial heat transfer fluids such as water, ethylene glycol, or engine oil to produce a new class of engineered fluids with high thermal conductivity. Nanofluids are this new class of heat transfer fluids and are engineered by suspending nanometer-sized particles in conventional heat transfer fluids. The average size of particles used in nanofluids is below 50 nm. The author coined the term nanofluids for this new class of heat transfer fluids (Choi, 1995).

It should be noted that in today's science and technology, "size does matter." Maxwell's concept of enhancing the thermal conductivity of fluids by dispersing solid particles is old, but what is new and innovative with the concept of nanofluids is the idea of using the nanometer-sized particles that have become available to investigators only recently.

5 TECHNOLOGY FOR PRODUCTION OF NANOPARTICLES AND NANOFLUIDS

Modern fabrication technology provides great opportunities to actively process materials at the micro- and nanometer scales. Nanostructured or nanophase materials are made of nanometer-sized substances engineered on the atomic or molecular scale to produce either new or enhanced physical properties not exhibited by conventional bulk solids. All physical mechanisms have a critical length scale, below which the physical properties of materials are changed. Therefore, particles <100 nm exhibit properties different from those of conventional solids. The noble properties of nanophase materials come from the relatively high surface-area-to-volume ratio that is due to the high proportion of constituent atoms residing at the grain boundaries. The thermal, mechanical, optical, magnetic, and electrical properties of nanophase materials are superior to those of conventional materials with coarse grain structures. Consequently, the research and development of nanophase materials has drawn considerable attention from material scientists and engineers alike (Duncan and Rouvray, 1989).

Much progress has been made recently in the production of nanophase materials, and current nanophase technology can produce large quantities of powders with average particle sizes of about 10-nm. Several "modern" nanophase materials have been prepared by physical gas-phase condensation or chemical synthesis techniques (Gleiter, 1989). The gas-phase condensation process involves the evaporation of a source material and the rapid condensation of vapor into nanometer-sized crystallites or loosely agglomerated clusters in a cool, inert, reduced-pressure atmosphere (Kimoto et al., 1963; Granqvist and Buhrman, 1976). A chemistry-based solution-spray conversion process starts with water-soluble salts of source materials. The solution is then turned into an aerosol and dried by a spray-drying system. Rapid vaporization of the solvent and rapid precipitation of the solute keeps the composition identical to that of the starting solution. The precursor powder is then placed in a fluidized-bed reactor to evenly pyrolyze the mixture, drive off volatile constituents, and yield porous powders with a uniform homogeneous fine structure (Ashly, 1994). A third technique is to generate nanophase materials by condensation of metal vapors during rapid expansion in a supersonic nozzle (Hill, et al., 1963; Andres, et al., 1981; Brown, et al., 1992).

If powders are produced by one of these processes, some agglomeration of individual particles may occur. It is well known, however, that these agglomerates, which are typically 1 μm or so in size, require little energy to fracture into smaller constituents, and thus it is possible they will not present a problem in this application. If, however, agglomeration is a problem, it would prevent realization of the full potential of the high surface areas of nanoparticles in nanofluids. Another promising technique for producing nonagglomerating nanoparticles involves condensing nanophase powders from the vapor phase directly into a flowing low-vapor-pressure fluid. This approach was developed in Japan 20 years ago by Akoh et al. (1978) and is called the VEROS (Vacuum Evaporation onto a Running Oil Substrate)

technique. VEROS has been essentially ignored by the nanocrystalline-materials community because of difficulties in subsequently separating the particles from the fluids to make dry powders or bulk materials. A modification of the VEROS process was developed recently in Germany (Wagener et al., 1997). Figure 2 is a schematic diagram of the direct evaporation system built at ANL and based on this modified process (Eastman et al., 1997).

Two techniques are used to make nanofluids: the single-step direct evaporation method, which simultaneously makes and disperses the nanoparticles directly into the base fluids, and the two-step method which first makes nanoparticles and then disperses 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. For nanofluids prepared by the two-step method, dispersion techniques such as high shear and ultrasound can be used to create various particle/fluid combinations.

Nanophase Technologies Corporation, a former spin-off company of ANL, has already scaled up the gas condensation technique to produce large quantities of nanoparticles. Therefore, nanopowders produced in bulk at low prices can be used to make nanofluids by the two-step method. Although this technique works well for oxide nanoparticles, it is not as effective for metal nanoparticles such as copper, presumably due to greater sensitivity to the effects of agglomeration for dense particles such as metals than for lighter particles such as oxides. For nanofluids containing high conductivity metals, it is clear that the single-step direct evaporation technique is preferable to gas-condensation processing. We are currently working with an industrial partner to test the feasibility of scaling-up the direct-evaporation process to envisioned production level quantities.

ANL has already produced oxide nanofluids by the two-step technique and metal nanofluids by the single-step technique to conduct proof-of-concept tests (Eastman et al., 1997). In particular, it was demonstrated that stable suspensions can be achieved by maintaining the particle size below a threshold level.

6 THEORETICAL STUDY OF NANOFLUID THERMAL CONDUCTIVITY

Because of the absence of a theory for the thermal conductivities of nanofluids, an existing model that was developed for conventional solid/liquid systems with fine particles was used to estimate the effective thermal conductivities of nanofluids. Hamilton and Crosser (1962) developed a model to determine the effective thermal conductivities of two-component mixtures as a function of the conductivities of the pure materials, the composition of the mixture, and the shape of the dispersed particles. This model shows that nonspherical shapes (all other circumstances being the same) will increase thermal conductivity above that of spherical particles.

With the Hamilton and Crosser model applied to copper nanoparticles in water, the effective thermal conductivity of the copper/water system was estimated. The effects of particle volume fraction and shape on the thermal conductivity ratio for a copper-water system are plotted in Fig. 3. The results clearly show that the thermal conductivity of the fluid/particle

system depends on both particle volume fraction and the shape. Assuming that the sphericity (defined as the ratio of the surface area of a sphere with a volume equal to that of the particle to the surface area of the particle) of copper nanoparticles is 0.3, the thermal conductivity of water can be enhanced by a factor of 1.5 at the low nanoparticle volume fraction of 5%. This finding demonstrates theoretically the feasibility of nanofluids, i.e., metallic nanoparticles are capable of significantly increasing the thermal conductivity of conventional heat transfer fluids.

7 EXPERIMENTAL STUDY OF NANOFLUID THERMAL CONDUCTIVITY

The thermal conductivities behavior of nanofluids with low particle concentrations (1-5 vol.%) was also studied experimentally. A test apparatus based on the transient hot-wire technique was designed and fabricated to measure the thermal conductivities of nanofluids. Thermal conductivities of four oxide nanofluids were measured. In particular, water and ethylene-glycol- based nanofluids, containing copper oxide and aluminum oxide nanoparticles, were tested (Lee et al., 1998).

The experimental results show that these nanofluids have substantially higher thermal conductivities than the same liquids without nanoparticles. For example, a 20% improvement in the thermal conductivity of ethylene glycol was seen when 4 vol.% copper oxide was dispersed in this fluid (see Fig. 4). Recent measurements show that less than 1 vol.% copper nanoparticles in ethylene glycol improve the effective thermal conductivity 40%.

In the low-volume- fraction range tested, the thermal conductivity ratios increase almost linearly with volume fraction, but with different rates of increase for each system. The experimental data also show that the thermal conductivities of nanofluids depend on the thermal conductivities of both the base fluids and particles.

Comparisons between experimental results and predictions of the model developed by Hamilton and Crosser (1962) show that the model can predict the thermal conductivity of nanofluids containing large agglomerated particles. However, the model predictions begin to diverge from the experimental data at low volume fractions. This strongly suggests that not only particle shape but also size is considered to be dominant in enhancing the thermal conductivity of nanofluids (Lee et al., 1998).

In our study, the thermal conductivities of stationary, rather than flowing, nanofluids were considered. Several investigators have reported augmentation of the effective thermal conductivities of suspensions with millimeter-sized polystyrene particles under laminar flow (Ahuja 1975; Sohn and Chen 1981). Therefore, we expect that the effective thermal conductivities of nanofluids under flow conditions might be higher than those seen in the present experimental results. Hence, heat transfer tests to assess the thermal performance of nanofluids under controlled flow conditions have been conducted.

8 EXPERIMENTAL STUDY OF NANOFLUID HEAT TRANSFER

Increased thermal conductivity will result in higher heat transfer than that of the base (pure) fluid without dispersed nanoparticles. Measurements of the heat transfer coefficients of nanofluids have shown that the heat transfer capability of water increased by 15% with a dispersion of less than 1 vol.% copper oxide nanoparticles (Zussman, 1997). Recently, we have seen about 80% improvements in heat transfer with the dispersion of less than 3 vol.% alumina nanoparticles. It should be noted that the observed heat transfer rates of nanofluids are much higher than those predicted by conventional heat transfer correlations, even when changes in thermophysical properties such as thermal conductivity, density, specific heat, and viscosity are considered. It appears that the effect of particle size and number becomes predominant in enhancing heat transfer in nanofluids.

All of these results on thermal conductivity and heat transfer enhancement were from nanofluids containing metallic oxide nanoparticles. Even greater effects are expected for nanofluids that contain metal nanoparticles (such as Cu, Ag) rather than oxides. Therefore, there is great potential to "engineer" ultra-energy-efficient heat transfer fluids by choosing the nanoparticle material, as well as by controlling particle size and loading. Therefore, we will measure the heat transfer coefficient for metal particles in ethylene glycol or oil.

9 DEVELOPMENT OF NANOFLUIDS WITH INDUSTRIAL PARTNERS

ANL's cooperative projects with industrial partners are focused on (1) identification of potential applications of nanofluids; (2) estimation of the potential benefits of nanofluids based on heat transfer and pressure drop data; and (3) development of techniques for scaling up production of oxide and metal nanofluids economically.

Potential Applications of Nanofluids

There is great industrial interest in nanofluids. Since the appearance of an article on nanofluids in ANL's "Tech Transfer Highlights" (Zussman, 1997), more than 20 companies have contacted ANl, showing great interest and suggesting future interactions involving a number of possible applications of nanofluids. These companies include both heat transfer fluid manufacturers and end users. As a further indication of the potential impact of nanofluids technology on industry, the November 1997 issue of "High-Tech Materials Alert" by John Wiley & Sons, Inc., featured ANL's nanofluids project on page 1 (Katz, 1997). Also, an article on heat transfer fluids, including nanofluids, has appeared in the September 1998 issue of Chemical Engineering magazine (read by more than 100,000 chemical engineers and allied professionals globally) (Shanley, 1998). This great industrial interest shows that nanofluids can be used for a wide variety of industries ranging from transportation, HVAC, and energy production and supply to electronics, textiles, and paper production. All of these industries are limited by heat transfer and so have a strong need for improved fluids that can transfer heat more efficiently.

Potential Benefits of Nanofluids

The impact of this new heat transfer technology is expected to be great, considering that heat exchangers are ubiquitous in all types of industrial applications and that heat transfer performance is vital in numerous multibillion-dollar industries. There is now great industrial interest in nanofluids. Some of the specific potential benefits of nanofluids are described below.

Improved Heat Transfer and Stability: Because heat transfer takes place at the surface of the particle, it is desirable to use a particle with a large surface area. Nanoparticles provide extremely high surface areas for heat transfer and therefore have great potential for use in heat transfer. The much larger relative surface areas of nanophase powders, when compared with those of conventional micrometer-sized powders, should markedly improve the heat transfer capabilities and stability of the suspensions.

Reduced Pumping Power: In heat exchangers that use conventional fluids, the heat transfer coefficient can be increased only by significantly increasing the velocity of the fluid in the heat transfer equipment. However, the requited pumping power increases significantly with increasing velocity. For a nanofluid flowing in the same heat transfer equipment at a fixed velocity, enhancement of heat transfer due to increased thermal conductivity can be estimated. For example, to improve the heat transfer of a conventional fluid by a factor of 2, pumping power must be increased by a factor of about 10. However, if a nanoparticle-based fluid with a thermal conductivity ≈3 times that of a conventional fluid were used in the same heat transfer equipment, the rate of heat transfer would be doubled (Choi, 1995). Therefore, the potential savings in pumping power is significant with nanofluids.

Minimal Clogging: ANL researchers are developing advanced fluids for industrial applications, including district heating and cooling systems (Choi and Tran, 1991; Choi et al., 1992a and 1992b). One problem identified in this R&D program was that micrometer-sized particles cannot be used in practical heat transfer equipment because of severe clogging problems. However, nanophase metals are believed to be ideally suited for applications in which fluids flow through small passages, because the metallic nanoparticles are small enough that they are expected to behave like molecules of liquid. This will open up the possibility of using nanoparticles even in microchannels for many envisioned high-heat-load applications.

Miniaturized Systems: Nanofluid technology will support the current industrial trend toward component and system miniaturization by enabling the design of smaller and lighter heat exchanger systems. Miniaturized systems will reduce heat transfer fluid inventory.

Cost and Energy Savings: Successful employment of nanofluids will result in significant energy and cost savings because heat exchange systems can be made smaller and lighter.

Scale-Up Studies of Nanofluid Production

ANL has initiated scale-up studies of nanofluid production by the direct evaporation technique. A system for evaporating nanoparticles into low-vapor-pressure fluids such as pump oil already exists at ANL. Therefore, the objectives of these studies are not only to scale up the

existing system for such fluids but also to develop a method for direct evaporation of nanoparticles into high-vapor-pressure fluids such as water.

10 FUTURE RESEARCH ON FUNDAMENTALS AND APPLICATIONS OF NANOFLUIDS

In less than three years since the seminal work by Choi (1995) reported the concept of nanofluids, interest in this area has grown. However, investigators are having difficulty in understanding the anomalous behavior of nanofluids in regard to thermal conductivity and convection heat transfer coefficient. The thermal conductivity anomaly is that experimental thermal conductivities of nanofluids increase relative to those of base fluids, whereas the theoretical thermal conductivities of nanometer-scale materials (including nanoparticles) dramatically decrease relative to those of the bulk materials used to produce nanoparticles (Majumdar, 1998). Regarding the heat transfer anomaly, despite the remarkable reduction in the thermal conductivities of nanoparticles, the experimental heat transfer coefficients of nanofluids are higher than those predicted with existing correlations.

Such a large enhancement in thermal conductivity and heat transfer of nanofluids cannot be explained by the classical theories and models currently used for traditional solid/liquid suspensions (Maxwell, 1873; Hashin and Shtrikman, 1962; Jeffrey, 1973; Jackson, 1975; Davis, 1986; Bonnecaze and Brady, 1991; Lu and Lin, 1996). All of the previous theories of the thermal conductivity and heat transfer of solid/liquid systems were developed for fluids containing relatively large particles (three to six orders of magnitude larger than nanoparticles). Only recently have nanoparticles of 50 nm or less become available to investigators. Experiments have shown that all existing theories, models, and correlations for thermal conductivity and convective heat transfer are very limited and often contradictory when applied to fluids containing nanoparticles.

It appears that we have discovered an anomalous behavior of fluids containing astronomical numbers of extremely small particles (particle density is about $10^{23}/m^3$). Although nanofluids hold great potential for improving heat transfer in many applications, their underlying fundamentals are not understood because the particles are drastically different from conventional particles.

We need to investigate the fundamentals of nanofluids to discover and understand the missing energy transport mechanisms. To our knowledge, no fundamental studies have been conducted on the thermal conductivity and heat transfer of nanofluids. Based on an understanding of the physics of nanofluid flows, we need to develop computational models of nanofluid flows. The developed models can then be used to predict the heat and momentum transport characteristics of nanofluid flows, and these tools can be integrated into the nanofluid design process.

Our future research will focus on providing answers to such fundamental questions as:

- What allows the formation of stable suspensions?

- What gives the ability to significantly increase thermal conductivity?
- What are the mechanisms for the dramatically enhanced heat transfer?

Thermal conductivity and heat transfer of nanofluids depend not only on forces acting on nanoparticles but also on particle motion and on interaction with turbulent eddies. At present, a fundamental and quantitative understanding of the thermal conductivity and heat transfer mechanisms is lacking. After successful completion of these fundamental studies, we will understand the anomalous behavior of nanofluids.

Our results will provide for the first time the data bases needed to answer these questions. A thermal conductivity model of nanofluids and computational models for the convective heat transfer coefficient of nanofluid flows will be developed and validated. Comparison of experimental data with numerical data will reveal the key parameters missing in existing theories and an understanding of the fundamental mechanisms of the thermal conductivity and heat transfer enhancement of nanofluids. A better understanding of the nanofluid heat transfer enhancement mechanisms will lead to a series of important recommendations for nanofluid design and engineering for industry. In short, scientists will be able to explain the anomalous behavior of nanofluids, and engineers will be able to design ultra-energy-efficient nanofluids.

In addition to these fundamental issues, we need to address a number of concerns related to the use of nanofluids, including clogging, fouling, corrosion, abrasion, compatibility, long-term stability, and scale-up. For example, we need to conduct experiments to show that clogging and fouling will not be problems. If corrosion is a problem, we need to find the nanoparticle material compatible with the thermal system. A recent paper (Hu and Dong, 1998) shows that titanium oxide nanoparticles in oil, unlike conventional particles, reduce the friction coefficient and increase wear resistance. Therefore, abrasion may not be a problem because the nanoparticles have less kinetic energy than do the larger conventional particles. Compatibility of nanoparticle materials with existing heat transfer fluids should be explored, especially when the existing fluids already contain a number of elements for freeze prevention, corrosion inhibition, and electrolysis. Long-term stability of the nanofluids and production scale-up issues could be problems in the commercialization of nanofluids.

11 CONCLUDING REMARKS

Downscaling, or miniaturization, has been the major trend in modern science and technology, and is also a unique feature of the author's research journey at Argonne National Laboratory (ANL). The journey started with large-scale flow and heat transfer experiments when many individuals still adhered to the idea of "bigger is better." Because large-scale experiments were too costly to run in times of reduced funding, the author sought an alternative to large-scale tests. Eventually, his research on advanced fluids and microchannel resulted in the invention of nanofluids, probably the world's most advanced heat transfer fluids and capable of flow in microchannels.

Modern nanotechnology provides great opportunities to process and produce materials with average crystallite sizes below 50 nm. Recognizing an opportunity to apply this emerging

nanotechnology to established thermal energy engineering, ANL has developed the concept of nanofluids. Maxwell's concept of enhancing the thermal conductivity of fluids by dispersing solid particles is old, but the concept of nanofluids, containing nanometer-sized particles that have become available to investigators only recently, is a new and innovative idea.

ANL's nanofluids team has performed, with internal discretionary funding, research on nanofluids and demonstrated for the first time in the world the feasibility of the nanofluid concept. The Laboratory has produced nanofluids by two techniques and conducted proof-of-concept tests. It was demonstrated that stable suspensions of oxide and metallic nanoparticles in conventional heat transfer fluids can be achieved by maintaining the particle size below a threshold level. Also, experimental studies with oxide nanofluids revealed high thermal conductivities and heat transfer coefficients compared to those of conventional fluids. Even greater effects are demonstrated in metallic nanofluids at very low volume fractions of nanoparticles.

ANL has worked with industrial partners to develop nanofluids for industrial applications. Nanofluid technology is expected to positively affect a wide variety of industrial sectors, including the transportation, HVAC, chemical, and fiber manufacturing industries. The envisioned benefits of nanofluids include improved heat transfer, improved suspension stability, decreased pumping power need, miniaturized systems, reduced heat transfer fluid inventories, minimal clogging in microchannels, and cost and energy savings.

Investigators at the frontier of nanofluids research have been intrigued by the anomalous behavior of nanofluids in thermal conductivity and convection heat transfer coefficient. We need to understand the missing energy transport mechanisms in nanofluids. Understanding the fundamentals of energy transport in nanofluids is important for developing extremely energy-efficient nanofluids for a range of heat transfer applications. To our knowledge, no fundamental studies have been carried out on the thermal conductivity and heat transfer of nanofluids. Thus, the invention of nanofluids presents new opportunities and challenges for thermal scientists and engineers.

ACKNOWLEDGMENTS

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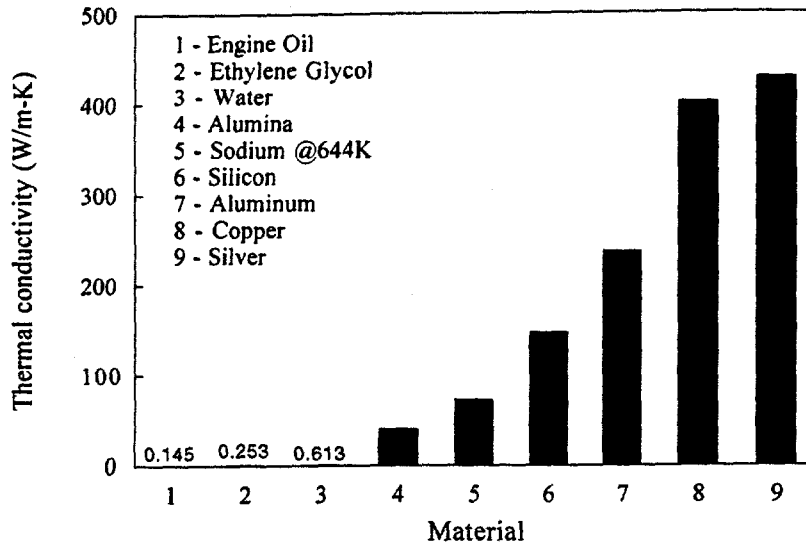
Fig. 1. Thermal conductivity of typical materials (at 300 K unless otherwise noted).
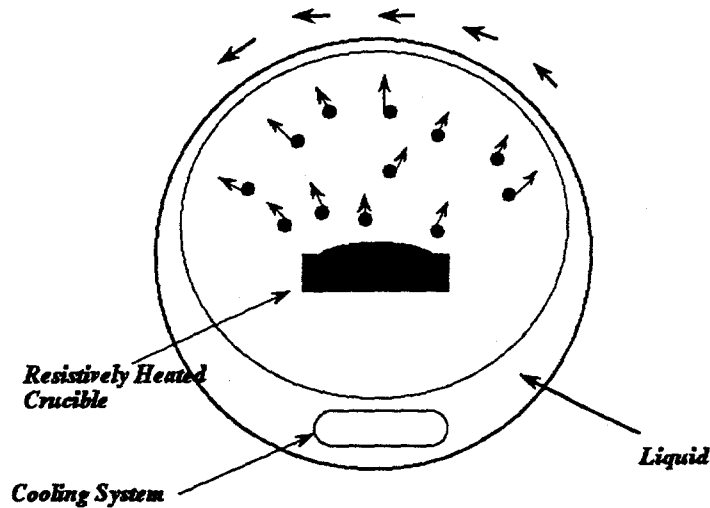

Fig. 2. Schematic diagram of nanofluid production system designed for direct evaporation of nanocrystalline particles into low-vapor-pressure liquids. The liquid is in a cylinder that is rotated to continually transport a thin layer of liquid above a resistively-heated evaporation source. The liquid is cooled to prevent an undesirable increase in vapor pressure due to radiant heating during evaporation.
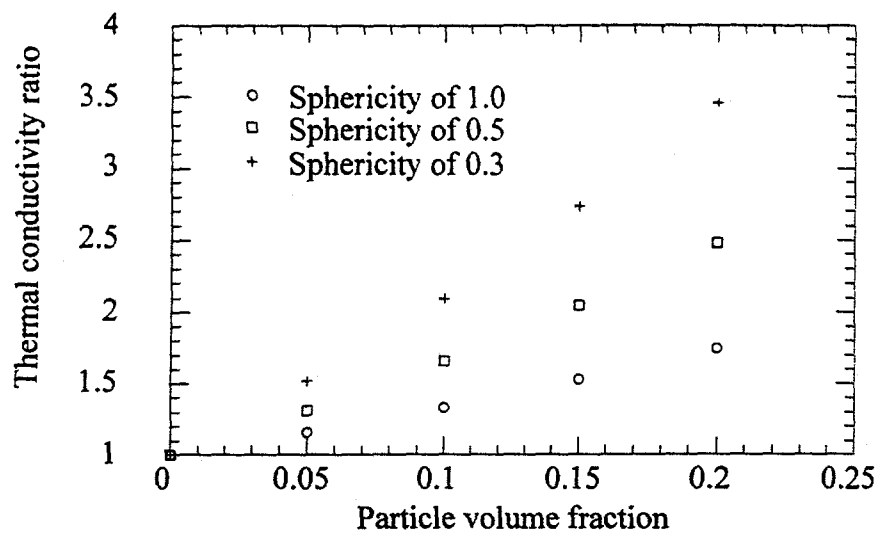
Fig. 3.   Effect of particle volume fraction and sphericity on thermal conductivity ratio
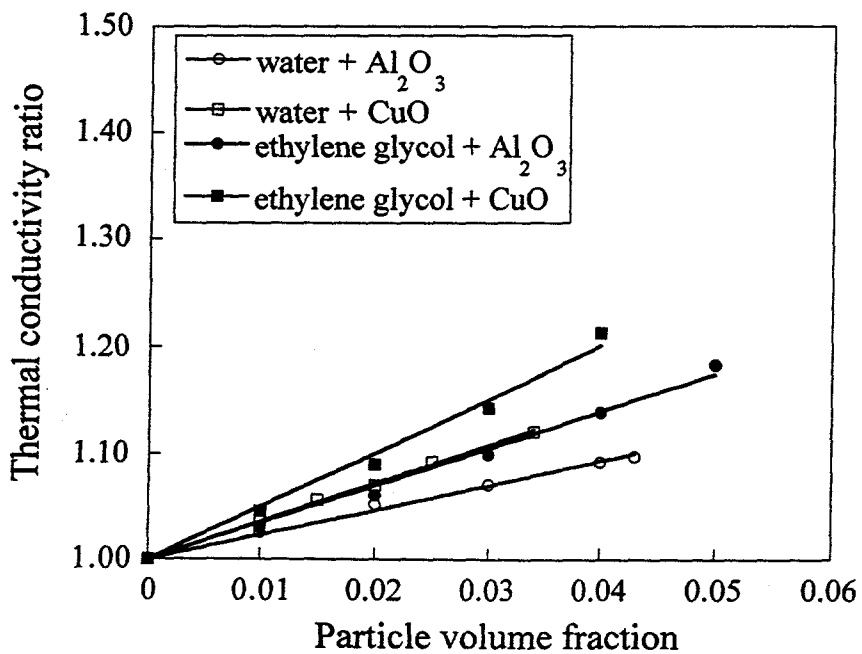for copper/water system.

Fig. 4.   Thermal conductivity of water and ethylene glycol
improves with increasing volume fraction of copper oxide
or aluminum oxide nanoparticles dispersed in base fluids.