Nanofluids for thermal transport

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Nanofluids, i.e. fluid suspensions of nanometer-sized solid particles and fibers, have been proposed as a route for surpassing the performance of heat transfer liquids currently available. Recent experiments on nanofluids have indicated significant increases in thermal conductivity compared with liquids without nanoparticles or larger particles, strong temperature dependence of thermal conductivity, and significant increases in critical heat flux in boiling heat transfer. Some of the experimental results are controversial, e.g. the extent of thermal conductivity enhancement sometimes greatly exceeds the predictions of wellestablished theories. So, if these exciting results on nanofluids can be confirmed in future systematic experiments, new theoretical descriptions may be needed to account properly for the unique features of nanofluids, such as high particle mobility and large surface-to-volume ratio.

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³Department of Materials Science and Engineering, and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana-Champaign, 1304 W. Green St., USA E-mail: d-cahill@uiuc.edu Cooling is one of the most important technical challenges facing many diverse industries, including microelectronics, transportation, solid-state lighting, and manufacturing. Technological developments such as microelectronic devices with smaller (sub-100 nm) features and faster (multi-gigahertz) operating speeds, higher-power engines, and brighter optical devices are driving increased thermal loads, requiring advances in cooling. The conventional method for increasing heat dissipation is to increase the area available for exchanging heat with a heat transfer fluid. However, this approach requires an undesirable increase in the thermal management system's size. There is therefore an urgent need for new and innovative coolants with improved performance. The novel concept of 'nanofluids' - heat transfer fluids containing suspensions of nanoparticles – has been proposed as a means of meeting these challenges¹.

Nanofluids are solid-liquid composite materials consisting of solid nanoparticles or nanofibers with sizes typically of 1-100 nm suspended in liquid. Nanofluids have attracted great interest recently because of reports of greatly enhanced thermal properties. For example, a small amount (<1% volume fraction) of Cu nanoparticles or carbon nanotubes dispersed in ethylene glycol or oil is reported to increase the inherently poor thermal conductivity of the liquid by 40% and 150%, respectively^{2,3}. Conventional particle-liquid suspensions require high concentrations (>10%) of particles to achieve such enhancement. However, problems of rheology and stability are amplified at high concentrations, precluding the widespread use of conventional slurries as heat transfer fluids. In some cases, the observed enhancement in thermal conductivity of nanofluids is orders of magnitude larger than predicted by well-established theories. Other perplexing results in this rapidly evolving field include a surprisingly strong temperature dependence of the thermal conductivity^{4,5} and a three-fold higher critical heat flux compared with the base fluids^{6,7}.

These enhanced thermal properties are not merely of academic interest. If confirmed and found consistent, they would make nanofluids promising for applications in thermal management. Furthermore, suspensions of metal nanoparticles are also being developed for other purposes, such as medical applications including cancer therapy⁸. The interdisciplinary nature of nanofluid research presents a great opportunity for exploration and discovery at the frontiers of nanotechnology⁹.

Synthesis of nanofluids

The optimization of nanofluid thermal properties requires successful synthesis procedures for creating stable suspensions of nanoparticles in liquids. Depending on the requirements of a particular application, many combinations of particle materials and fluids are of potential interest. For example, nanoparticles of oxides, nitrides, metals, metal carbides, and nonmetals with or without surfactant molecules can be dispersed into fluids such as water, ethylene glycol, or oils. Studies to date have used one or more of several possible methods for nanoparticle production and dispersion. Here, we briefly mention the techniques that, so far, have been most commonly used.

Several studies, including the earliest investigations of nanofluids, used a two-step process¹⁰ in which nanoparticles or nanotubes are first produced as a dry powder, often by inert gas condensation¹¹ (Fig.1, middle). Chemical vapor deposition has also been used to produce materials for use in nanofluids, particularly multiwalled carbon nanotubes³. The nanoparticles or nanotubes are then dispersed into a fluid in a second processing step. Simple techniques such as ultrasonic agitation or the addition of surfactants to the fluids are sometimes used to minimize particle aggregation and improve dispersion behavior. Such a two-step process works well in some cases, such as nanofluids consisting of oxide nanoparticles dispersed in deionized water¹⁰. Less success has been found when producing nanofluids containing heavier metallic nanoparticles¹². Since nanopowder synthesis techniques have already been scaled up to industrial production levels by several companies¹³, there are potential economic advantages in using two-step synthesis methods that rely on the use of such powders.

Single-step nanofluid processing methods have also been developed. For example, nanofluids containing dispersed metal nanoparticles^{2,11} have been produced by a 'direct-evaporation' technique¹⁴ (Fig. 1, left). As with the inert gas condensation technique, this involves the vaporization of a source material under vacuum conditions. An advantage of this technique is that nanoparticle agglomeration is minimized, while a disadvantage is that only low vapor pressure fluids are compatible with the process. Various single-step chemical synthesis techniques can also be employed to produce nanofluids. For example, a technique developed by Brust and coworkers¹⁵ for producing metallic nanoparticles by the reduction of metal salts has been used widely to produce colloidal suspensions in various solvents



Fig. 1 Transmission electron micrographs showing (left) Cu nanofluids² (© 2001 American Institute of Physics), (middle) CuO nanoparticles¹⁰ (© 1999 MRS), and (right) alkanethiol terminated AuPd colloidal particles¹⁶ (© 2002 American Physical Society) used in studies of interfacial resistance. CuO particles show significant clustering associated with synthesis techniques and subsequent agglomeration. AuPd colloids show the best dispersion and very narrow size distribution.

for a wide range of applications, including studies of thermal transport¹⁶ (Fig. 1, right). Excellent control of size and very narrow size distributions can be obtained by using such methods.

Thermal transport in stationary fluids

Key features of nanofluids that have been reported so far include thermal conductivities exceeding those of traditional solid/liquid suspensions^{2,3}; a nonlinear relationship between thermal conductivity and concentration in the case of nanofluids containing carbon nanotubes³; strongly temperature-dependent thermal conductivity⁴; and a significant increase in critical heat flux in boiling heat transfer^{6,7,17}. Each of these features is highly desirable for thermal systems; a stable and easily synthesized fluid with these attributes and acceptable viscosity would be a strong candidate for the next generation of liquid coolants.

Published reports of how the thermal conductivity of the nanofluid varies as a function of nanoparticle loading are summarized in Fig. 2. Early experimental studies of the thermal transport properties of nanofluids focused on changes in properties created by high concentrations of oxide nanoparticles. Masuda *et al.*¹⁸ reported a 30% increase in the thermal conductivity of water with the addition of 4.3 vol.% Al_2O_3 nanoparticles. A subsequent study by Lee *et al.*¹⁰ also examined the behavior of Al_2O_3 nanoparticles in water, but



Fig. 2 Relative increase in the thermal conductivity as a function of the volume fraction of nanoparticles^{2,4,5,10,19,21,23,45}. The lower dashed line is the prediction from effective medium theory for well-dispersed suspensions of highly thermally conductive nanoparticles; the upper dashed line is the prediction for random-close-packed aggregates of nanoparticles. Most of the data is reasonably well described by effective medium theory. The most anomalous results (furthest left and above the dashed lines) for Cu and Au nanoparticle suspensions are^{2,45}, respectively.

observed only a 15% enhancement in thermal conductivity at the same nanoparticle loading. These differences in behavior were attributed to differences in average particle size in the two sets of samples. The Al₂O₃ nanoparticles used by Masuda et al. had an average diameter of 13 nm, compared with 33 nm in the study by Lee et al. Xie and coworkers^{19,20} found an intermediate result, i.e. the thermal conductivity of water is enhanced by approximately 20% by a nanoparticle loading of 5 vol.%. The same group found similar results for SiC²¹. Lee et al. observed only a modest improvement in the thermal conductivity of nanofluids containing CuO compared with Al₂O₃, but Wang and coworkers²² reported a surprising 17% increase in thermal conductivity for a loading of just 0.4 vol.% CuO nanoparticles in water. The thermal conductivity of an ethylene glycol-based nanofluid was shown² to be increased by up to 40% when loaded with approximately 0.3 vol.% Cu nanoparticles of mean diameter ~10 nm. Patel and coworkers⁵ observed increases in fluid thermal conductivity of up to 21% in their recent study on the behavior of Au and Ag nanoparticles dispersed in water and toluene, but, astonishingly, were able to achieve these results at extremely low nanoparticle loadings of just 0.011 vol.%.

To the best of our knowledge, the anomalously large increases in thermal conductivity observed for CuO nanofluids²², Cu nanofluids², and Au and Ag nanofluids⁵ have not been confirmed independently. In fact, a recent attempt at duplicating the Cu nanofluid results² appears to have failed: in this case, the Cu nanoparticles were larger (50 nm) but no significant enhancement in thermal conductivity was observed with Cu nanoparticle loadings of up to 0.5 vol.%²³.

A potentially important development is the recent observation of a strong temperature dependence of enhancement in thermal conductivity for both high concentrations of oxide nanoparticles⁴ and extremely low concentrations of metal nanoparticles⁵. In both nanofluid systems, a two- to four-fold increase in the enhancement of thermal conductivity was observed over a small temperature range (20-50°C). If confirmed, and if this temperature dependence occurs over a wide temperature range, then this property could make nanofluids particularly attractive for applications at elevated temperatures.

The largest increases in thermal conductivity have been observed in suspensions of carbon nanotubes, which, in addition to high thermal conductivity, have very high aspect ratio (Fig. 3). Since carbon nanotubes form a highly entangled



Fig. 3 Scanning electron micrographs of carbon nanotube samples typical of those used in suspensions and composites: (a) single-walled carbon nanotubes obtained by arc discharge and (b) multiwalled carbon nanotubes obtained by chemical vapor deposition growth. (Courtesy of P. M. Ajayan, Rensselaer Polytechnic Institute.)

fiber network, they are not mobile, as demonstrated by viscosity measurements²⁴, and thus their effect on the thermal transport of fluid suspensions is expected to be similar to that of polymer composites. The first reported work on a single-walled carbon nanotube-polymer epoxy composite, by Biercuk et al.²⁵ (Fig. 3a), demonstrated a 125% increase in thermal conductivity at 1 wt.% nanotube loading at room temperature. Biercuk et al. also observed a thermal conductivity that increases with increasing temperature. Choi et al.³ measured thermal conductivities of oil suspensions containing multiwalled carbon nanotubes (Fig. 3b) up to 1 vol.% loading and found similar behavior, in this case a 160% enhancement. Interestingly, the conductivity enhancement increased more rapidly than a linear dependence on nanotube loading. Thus, interactions of thermal fields associated with different fibers may become important as the loading approaches 1 vol.%.

Several studies of carbon nanotube suspensions have shown smaller enhancements in thermal conductivity: Xie *et al.*²⁶ measured carbon nanotube-organic liquid and water suspensions and found only 10-20% increases in thermal conductivity at 1 vol.%; Wen and Ding²⁷ found a ~25% enhancement in the conductivity at ~ 0.8 vol.% carbon nanotubes in water; and Assael and coworkers²³ found a maximum enhancement of 38% with 0.6 vol.% nanotubes in water. In Wen and Ding's work, the enhancement in the conductivity of the suspension increases rapidly with loading up to 0.2 vol.% and then begins to saturate. In agreement with Biercuk *et al.*²⁵, Wen and Ding observed increases in thermal conductivity with increasing temperature. However, these increases tended to saturate at *T* > 30°C.

Flow, convection, and boiling

Recently, the heat transfer coefficient of nanofluids in natural^{28,29} and forced flow³⁰⁻³² has been measured. Also,

Das *et al.*¹⁷ initiated experiments on the boiling characteristics of nanofluids. You *et al.*⁶ measured the critical heat flux in a pool of boiling Al_2O_3 -water nanofluid and reported an unprecedented three-fold increase over that of pure water. Subsequently, Vassallo *et al.*⁷ reported that silicawater nanofluid shows three-fold higher critical heat flux compared with base fluids.

In convective heat transfer in nanofluids, the heat transfer coefficient depends not only on the thermal conductivity but also on other properties, such as the specific heat, density, and dynamic viscosity of a nanofluid. At low volume fractions, the density and specific heat of nanofluids are expected, and have been observed³³, to be very similar to those characterizing the base fluid. Wang et al.³⁴ measured the viscosity of Al₂O₃-water nanofluids and showed that nanofluids have lower viscosities when the particles are more dispersed. They also found an increase of ~30% in viscosity at 3 vol.% Al_2O_3 , compared with that of water alone. However, the viscosity of the Al₂O₃-water nanofluid prepared by Pak and Cho³⁵ was three times higher than that of water. As expected, the viscosity of nanofluids depends on the methods used to disperse and stabilize the nanoparticle suspension. Xuan and Li³² measured the turbulent friction factor of water-based nanofluids containing Cu nanoparticles in a volume fraction range of 1.0-2.0. Interestingly, they found that the friction factor for the nanofluids is approximately the same as that of water.

Forced convection measurements by Eastman *et al.*³⁶ reported that the heat transfer coefficient of water containing 0.9 vol.% of CuO nanoparticles was improved by >15% compared with that of water without nanoparticles. Xuan and Li³² measured the convective heat transfer coefficient and friction factor of Cu-water nanofluids in turbulent flow. Their results show that a small amount (<2 vol.%) of Cu nanoparticles in deionized water improves convective heat transfer remarkably. For example, the convective heat transfer coefficient of a nanofluid containing 2.0 vol.% of Cu nanoparticles was improved by >39% compared with that of water without nanoparticles. In contrast to these studies, Pak and Cho³⁵ found that the convective heat transfer coefficient of water-based nanofluids with 3 vol.% Al_2O_3 and TiO_2 nanoparticles was 12% smaller than that of pure water when tested under the condition of constant average velocity. Putra *et al.*²⁸ studied natural convection of Al_2O_3 - and CuO-water nanofluids. Unlike conduction or forced convection, these natural convection experiments show a decrease in heat transfer.

The pool boiling experiments of Das *et al.*¹⁷ on Al₂O₃water nanofluids showed a deterioration of the pool boiling performance of nanofluids with increasing particle volume fraction. This deterioration is not attributed to a change in fluid properties by nanoparticles, but to a change in the boiler's surface characteristics by nanoparticles deposited on the rough surface of the boiler. You et al.⁶ measured the critical heat flux in pool boiling on a flat, square Cu surface immersed in Al₂O₃-water nanofluids and showed an unprecedented three-fold increase in critical heat flux over that of pure water. The average size of the departing bubbles increases and the bubble frequency decreases significantly in nanofluids compared with pure water. The remarkable results of You *et al.*⁶ are consistent with the more recent results of Vassallo et al.⁷, who conducted experiments with silica-water nanofluids. It is intriguing that nanoparticles at concentrations as low as 10⁻³ vol.% can trigger such a dramatic increase in critical heat flux; no existing model can explain such an effect.

Thermal conductivity of nanofluids: understanding and controversy

Since studies of nanofluid thermal conductivity have been more prevalent than studies of other heat transfer properties, we limit our discussion to thermal conductivity, i.e. heat transfer by conduction in stationary fluids. Nanofluids are composite materials and, therefore, any discussion of nanofluid thermal conductivity must begin with effective medium theories. Effective medium theories were introduced by Mossotti, Clausius, Maxwell, and Lorenz in the late 19th century, firmly established with the work of Bruggeman³⁷, and thoroughly investigated and applied in many fields of science and engineering since then³⁸.

We begin our discussion with the simplest case of spherical particles where interface effects are negligible. In other words, at this stage we do not consider the finite thermal conductance of the particle/fluid interface. In the limit of a small volume fraction of nanoparticles f all versions of the effective medium theory converge to the same solution and, in the limit of high thermal conductivity particles, predict that the nanofluid's thermal conductivity enhancement will be 3f. This prediction is a good approximation to the exact solution for finite thermal conductivity particles, as long as the thermal conductivity of the particle is >20 times the thermal conductivity of the fluid³⁹. As shown in Fig. 2, many experimental results on nanofluids are in reasonably good agreement with this prediction, e.g. the 26 nm SiC nanofluids and alumina-water nanofluids studied by Xie and coworkers²¹ and the aluminaethylene glycol nanofluids studied by Lee¹⁰. As we discuss below, the interface resistance between the nanoparticle and surrounding fluid will reduce the predictions of the effective medium theory. For particles on the order of 30 nm in diameter, however, we do not expect the reduction to be significant.

Many of the other results for high concentrations of nanoparticles can also be understood based on effective medium theory, if we allow for the possibility that the nanoparticles have clustered into small aggregates (Fig. 1, middle). Since an aggregate of nanoparticles occupies more space than the individual nanoparticles that make up the aggregate, the volume fraction of the aggregates is larger than the volume fraction of nanoparticles⁴⁰. A random close packing of spherical nanoparticles will have a relative density of approximately 60%. So, if the nanoparticles have aggregated, we can expect an enhancement in the thermal conductivity of approximately 3f/0.6, or 5f. Even larger enhancements are possible for more loosely packed clusters (Fig. 4). An enhancement in the thermal conductivity of approximately 5f is often observed²⁰. The thermal conductivity of the aggregate will, of course, be smaller than the thermal conductivity of the nanoparticle, but this reduction in conductivity - we estimate a factor of two reduction in thermal conductivity of the aggregate relative to the nanoparticle - will not be a significant factor if the conductivity of the nanoparticles is sufficiently large.

Effective medium theories for fiber composites are more complex, but the equations can be solved exactly for a high-



Fig. 4 Predictions from effective medium theory of the composite conductivity normalized by the conductivity of the matrix as a function of volume fraction f loading of high thermal conductivity spherical nanoparticles: solid squares – well-dispersed particles; circles – clusters of packed particles (60 vol.% particles); open squares – loosely packed clusters (40 vol.% particles).

aspect-ratio ellipsoid. As before, the predictions of effective medium theories converge to a common solution in the limit of a small volume fraction *f*. In this case, however, knowledge of the thermal conductivity and aspect ratio of the fiber are needed to make quantitative predictions for the thermal conductivity of the composite. For example, in the limit of high-aspect-ratio fibers, a simple geometrical analysis provides an estimate for the composite thermal conductivity Λ_{eff} assuming that the thermal resistance of the nanotube interfaces is negligible:

$$\Lambda_{eff} = f \Lambda_{fiber} < \cos^2 \theta > \tag{1}$$

where Λ_{eff} and Λ_{fiber} are the thermal conductivity of the composite and fiber, respectively, *f* is the fiber volume fraction, and θ is the angle between the direction of heat flow and the fiber axis. The brackets in eq 1 indicate an average over all fibers in the composite. Even for random fiber orientations ($\langle \cos^2 \theta \rangle = 1/3$) with $\Lambda_{fiber} = 3000$ W/m K, f = 0.01, eq 1 yields $\Lambda_{eff} = 10$ W/m K, which is ~15 times larger than the conductivity of water and ~50 times larger than the conductivity of an organic liquid. If realizable, nanofluids containing such fibers would have obvious technological applications. However, the largest enhancements observed by experiment have been about factor of two.

This lower-than-expected thermal conductivity is attributed to the thermal interfacial resistance R_k . The

interfacial conductance $G = 1/R_k$ is related to the heat flux J_Q and the temperature drop at the interface ΔT via:

 $J_Q = G \,\Delta T \,. \tag{2}$

A simple measure of the relative importance of interfacial resistance in the overall heat flow in a composite can be obtained from the equivalent thickness *h*, defined as the distance over which the temperature drop is the same as at the interface. This thickness is given by the ratio of fluid thermal conductivity Λ to the interfacial conductance, $h = \Lambda/G$.

The interfacial resistance between a nanotube and an organic material was recently determined via a combination of laser-heating experiments and molecular simulations⁴¹. In the experiment, an interfacial conductance of 12 MW/m²K was measured, and similar results were obtained from molecular dynamics simulations (Fig. 5). The equivalent matrix thickness for a low-conductivity organic matrix (~0.1 W/m K) for the above values of interfacial resistance is about 10 nm. This is indeed a large value. For example, two tubes separated by 1 nm of matrix material will be separated thermally to a degree equivalent to a layer of the matrix material that is 20 nm thick. Furthermore, even if tubes are in direct contact, they only interact with weak dispersion forces



Fig. 5 Snapshot of atomic positions of a carbon nanotube immersed in liquid octane. Molecular dynamics simulations show that weak van der Waals forces acting between the nanotube and the liquid provide only poor thermal coupling and, consequently, the interfacial resistance to the heat flow is very significant.



Fig. 6 The effective composite conductivity estimated from effective medium theory⁴², normalized by the conductivity of the matrix and plotted as a function of the fiber aspect ratio. The interfacial resistance is set equal to the thermal resistance of a layer of the matrix material that is five times the radius of the fiber. Other parameters are the thermal conductivity of the fiber, 3000 W/m K, and the thermal conductivity of the matrix, 0.15 W/m K.

and are expected to experience a large tube-tube contact resistance. The fact that both tube-matrix interface resistance and tube-tube contact resistance are large explains the lack of a percolation threshold in thermal transport²⁵.

The effects of the interface thermal resistance can be included in effective medium theories^{42,43}. The effective thermal conductivity as a function of the fiber aspect ratio for a typical carbon nanotube is shown in Fig. 6. When the aspect ratio is ~3000 we recover the full thermal conductivity enhancement predicted by eq 1. However, carbon nanotubes have lower aspect ratios. Also, in a suspension or composite, nanotubes are curved⁹ (Fig. 3), which further reduces their effective aspect ratio. The critical aspect ratio, α , needed to recover the prediction of eq 1 scales as:

$$\alpha_{critical} \sim \sqrt{\Lambda_{fiber}/G r}$$
(3)

where r is the fiber radius and G is the fiber-matrix interfacial conductance.

The interfacial thermal resistance also has an effect on spherical particle composites. In this case, in the limit of low volume fractions of nanoparticles, effective medium theory³⁹ predicts:

$$\Lambda_{eff} / \Lambda_{matrix} - 1 = 3f (\gamma - 1) / (\gamma + 2)$$
(4)
where γ is the ratio of the particle radius to the equivalent
matrix thickness *h*.

According to eq 4, when the particle radius becomes equal to the equivalent matrix thickness ($\gamma = 1$), there is no enhancement at all; for larger interfacial resistance ($\gamma < 1$), the addition of particles decreases the thermal conductivity of the composite. The thermal conductance of particle/matrix interfaces has also been measured recently: alumina particles in polymethyl methacrylate (PMMA) give $G = 30 \text{ MW/m}^2\text{K}$; Au alloy particles stabilized by alkane-thiol chemistries and suspended in toluene give $G = 15 \text{ MW/m}^2\text{K}$; and Au alloy particles stabilized by a variety of surfactants and suspended in water give $150 < G < 250 \text{ MW/m}^2\text{K}$ (Fig. 1, right)^{16,39,44}.

Evaluation of eq 3 is complicated by two factors: the correct choice for average particle radius and the correct choice of interface thermal conductance G. Typically, authors report the number-weighted average of the particle radius. But in eq 3, we must use the volume-weighted average of the particle radius³⁹. If the polydispersity is large, then the volume-weighted average radius will be significantly larger than the average radius. As reviewed above, the thermal conductance of particle-fluid interfaces is known in only a few cases. For example, we are not aware of any measurement of the thermal conductance of interfaces between oxide particles and fluids. Nevertheless, if we take $G = 200 \text{ MW/m}^2\text{K}$ as a typical value of the conductance of a particle-water interface and use a volume-weighted average radius of 30 nm, then $\gamma = 10$ and the effective medium prediction for the enhancement of the thermal conductivity by 3f will not be significantly decreased by the interface effects.

Thermal motion of nanoparticles has sometimes been proposed as a mechanism that could enhance the thermal conductivity of a nanofluid. For Brownian motion to be a significant contributor to the thermal conductivity, it would have to be a more efficient heat-transfer mechanism than thermal diffusion in the fluid. However, Keblinski et al.⁴⁰. using a simple analysis, have shown that thermal diffusion is much faster than Brownian diffusion, even within the limits of extremely small particles. In other words, thermal fields adjust to instantaneous particle positions and act as they do in an immobile particle composite. A number of other researchers have reached the opposite conclusion, including: (i) Xuan and Li³², whose work is hard to assess since their result for the thermal conductivity enhancement (their eq 13) has the wrong units; (ii) Kumar et al.45, who postulate that the Brownian motion mean free path of a nanoparticle in fluid is on the order of 1 cm, which is unphysical; and

(iii) Bhattacharya *et al.*⁴⁶, who, to obtain agreement with experiment, introduced an interparticle potential with a range of the order of one light year in their Brownian dynamics simulations.

A more recent idea relating to Brownian motion, put forward by Jang and Choi⁴⁷ and Prasher *et al.*⁴⁸, postulates the importance of the Brownian-motion-driven convection in the fluid, rather than the direct contribution to the thermal conductivity of the particle motion itself.

Keblinski *et al.*⁴⁰ have put forward other ideas to explain large thermal conductivity enhancements, including the possibility of larger thermal conductivity of an ordered liquid layer at particle interfaces and 'tunneling' of heat-carrying phonons from one particle to another. The same group of authors, in their subsequent simulation work, conclude that these mechanisms do not contribute significantly to heat transfer⁴⁹. Furthermore, interpretation of the cooling rates of Au nanoparticles suspended in water and organic solvents do not appear to require unusual thermophysical properties of the surrounding liquid to explain the experimental results¹⁶.

Outlook and future challenges

Many interesting properties of nanofluids have been reported in the past ten years. Thermal conductivity has received the most attention, but several groups have recently initiated studies of other heat-transfer properties. The use of nanofluids in a wide variety of applications appears promising, but the development of the field is hindered by: (i) the lack of agreement between results obtained in different laboratories; (ii) the often poor characterization of the suspensions; and (iii) the lack of theoretical understanding of the mechanisms responsible for the observed changes in properties. We conclude by outlining several important issues that we believe should receive greater attention in the future.

 Stability of the suspension is a crucial issue for both scientific research and practical applications. Particle aggregation and the formation of extended structures of linked nanoparticles may be responsible for much of the disagreement between experimental results and the predictions of effective medium theory. Simultaneous studies of thermal conductivity and viscosity may give additional insight. Some aggregation may be beneficial for suspensions of spherical nanoparticles, but, for nanotube suspensions and composites, aggregation is detrimental since bundling of nanotubes reduces the fiber aspect ratio. The size distribution of nanoparticles and nanoparticle aggregates in the suspensions is rarely reported. This lack of data can be attributed to the difficulty in properly characterizing high-concentration suspensions of nanoparticles, e.g. light scattering techniques work poorly or not at all at the high particle concentrations usually under consideration in nanofluid research. Cryogenic transmission electron microscopy might provide a powerful characterization method, but few materials laboratories are equipped to apply this technique and the structure of the nanofluids may change during cryofixation.

In most studies to date, sample sizes have been limited to less than a few hundred milliliters of nanofluid. Larger



Fig. 7 (top) Interfacial resistance between a carbon nanotube and liquid octane in units of equivalent matrix thickness plotted as a function of the fraction of nanotube carbon atoms with covalently attached octane molecules. Results were obtained from molecular dynamics simulations⁵⁰. The inset shows a functionalized carbon nanotube. (bottom) Axial conductivity of the carbon nanotube versus the fraction of functionalized nanotube carbon atoms.

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samples will be needed to test many properties of nanofluids in the future, particularly in assessing their potential for use in applications. Inert gas condensation synthesis, which has already been scaled up to produce large quantities of nanopowders, typically produces heavily agglomerated powders. Robust techniques for large-scale production of stable nanofluids are needed.

- High interfacial thermal resistance appears to be a critical factor in reducing the benefits of carbon nanotube fillers. Surface modification or functionalization may lead to stronger thermal conductivity enhancements. Scattering of thermal waves (phonons) by defects in tube crystal structure will, however, limit the benefit of the functionalization⁵⁰ by reducing the intrinsic thermal conductivity of the nanotubes (Fig. 7).
- Large increases in the critical heat flux in boiling heat transfer have been reported within the past year, and this

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phenomenon deserves thorough study. Thermal conductivity is probably not a critical issue for critical heat flux⁶, but the mechanisms that produce the increases are unknown at this time.

 Several studies have revealed significant increases in the heat transfer coefficient under forced flow conditions and in pool boiling experiments. However, other studies have yielded decreases in the heat transfer coefficient because of the addition of nanoparticles to the fluid. Heat transfer under forced flow conditions is most relevant regarding applications, so it is important to systematically identify factors leading to enhancement or deterioration of these convective heat flow characteristics. MT

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