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Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids)

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Abstract

Recent measurements on nanofluids have demonstrated that the thermal conductivity increases with decreasing grain size. However, such increases cannot be explained by existing theories. We explore four possible explanations for this anomalous increase: 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. We show that the key factors in understanding thermal properties of nanofluids are the ballistic, rather than diffusive, nature of heat transport in the nanoparticles, combined with direct or fluid-mediated clustering effects that provide paths for rapid heat transport.

Keywords: Thermal conductivity; Nanofluids; Molecular dynamics simulations; Ballistic heat transport

1. Introduction

It has long been recognized that suspensions of solid particles in liquids have great potential as improved heat-management fluids. The key idea is to exploit the very high thermal conductivities of solid particles, which can be hundreds or even thousands of times greater than those of conventional heat-transfer fluids such as water and ethylene glycol. In this context, numerous theoretical and experimental studies of the effective thermal conductivity of solid–particle suspensions have been conducted dating back to the classic work of Maxwell [1]. However, the vast majority of these studies have been confined to suspensions with millimeter- or micron-sized particles. Although such suspensions do indeed display the desired increase in thermal conductivity, they suffer from stability and rheological problems. In particular, the particles tend to quickly settle out of suspension and thereby cause severe clogging, particularly in mini and microchannels. However, a notable exception is provided by magnetic colloids [2] (involving solutions of ferromagnetic nanoparticles), which appear to be stable because of their very small particle size.

A novel approach to engineering fluids with better heat-transfer properties, based on the rapidly emerging field of nanotechnology, has recently been proposed [3]. In particular, it was demonstrated that solid nanoparticle colloids (i.e., colloids in which the grains have dimensions of ≈10–40 nm) are extremely stable and exhibit no significant settling under static conditions, even after weeks or months [4]. Furthermore, the enhancement of thermal-transport properties of such "nanofluids" was even greater than that of suspensions of coarse-grained materials [5]. For example, the use of Al_2O_3 particles ≈13 nm in diameter at 4.3% volume fraction increased the thermal conductivity of water under stationary conditions by 30% [6]. Use of somewhat larger particles (≈40 nm in diameter) only led to an increase of less than ≈10% at the same particle volume fraction [5]; more in accord with theoretical predictions

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Nomenclature

c_p	specific heat
D	particle diffusion constant
d	particle diameter
E	energy
$\mathbf{F}_{ij}$	force acting on atom i due to interactions with atom j
h	enthalpy
J_Q	thermal flux
k	thermal conductivity
k_B	Boltzmann constant
l	mean free path
n	empirical shape factor
$\mathbf{r}_{ij}$	vector connecting atoms i and j
T	temperature
t	time
V	particle volume fraction
$\mathbf{v}$	velocity vector

Greek symbols

γ	Gruneisen parameter
η	fluid viscosity
κ	excess-thermal-conductivity-enhancement coefficient, defined as $\kappa = k_{eff} - k_f/k_{HC} - k_f$
ρ	density
τ_D	time required for a particle to move by the distance equal to its size
τ_H	time required for heat to move in the liquid by the same distance
χ	thermometric conductivity, defined as $\chi = k/\rho c_p$

Superscripts

k	kinetic
p	potential

Subscripts

f	fluid
HC	Hamilton and Crosser theory
i	atom i
j	atom j
m	melting
p	particle

[7]. An even greater enhancement was recently reported for Cu nanofluids, where just a 0.3% volume fraction of 10 nm Cu nanoparticles led to an increase of up to 40% in thermal conductivity [8], a result that is more than an order of magnitude above the increase predicted by macroscopic theory. Currently, the origin of such remarkable increases in the thermal conductivity of nanofluids eludes theoretical understanding.

The existing understanding of the effective thermal conductivity of composites and mixtures is derived from continuum-level phenomenological formulations that typically incorporate only the particle shape and volume fraction as variables and assume diffusive heat transport in both liquid and solid phases; no effects of solid/liquid interfaces or particle mobility are taken into account. This approach, while providing a good description of systems with micrometer or larger-size particles, fails to describe thermal transport in nanofluids.

In this article we examine the various factors that could potentially be responsible for the inadequacy of macroscopic analysis in the description of heat transfer in nanofluids and expose new mechanisms capable of explaining the experimentally observed enhanced thermal conductivity of nanofluids. We limit our considerations to stationary nanofluids, because they already exhibit unusual thermal properties; we do not consider effects of macroscopic flow or convection on heat transfer in nanofluids [9,10]. The conclusions of our arguments are supported by the results of atomic-level molecular dynamics (MD) simulations that do not require the assumptions that underlie continuum-level formulations, and are thus well suited for studies of nanofluids. Our analysis and simulation results provide significant insights into the unusual heat transport properties of solid nanoparticle colloids and allow us to formulate the roadmap of an integrated experimental/modeling program toward developing a systematic understanding of the remarkable thermal transport properties of nanofluids.

2. Macroscopic theory of heat transport in composites

A large body of theoretical work is available on the effective thermal conductivity of two- or multi-component materials, e.g., the approaches of Hamilton and Crosser (HC) [7], and others [11–13]. The key assumption of such theoretical approaches is that the heat transport in each component is described by a diffusion equation [14], which in terms of the temperature field T assumes the form

$$\frac{\partial T}{\partial t} = \chi \nabla^2 T, \tag{1}$$

where χ is the thermometric conductivity defined as [14]

$$\chi = k/\rho c_p, \tag{2}$$

where k is thermal conductivity, ρ is the density, and c_p is the specific heat. Calculating the effective thermal conductivity of the composite material involves the solution of Laplace's equation (the diffusion

equation in the stationary state), with boundary conditions satisfying continuity of the thermal flux J_Q given by

$$\vec{J}_Q = -k\vec{\nabla}T. \tag{3}$$

Within such an approach, the HC theory, based on Maxwell's work on dielectric properties of composite materials, yields the following expression for the effective conductivity of a matrix (in our case the liquid) that contains a dispersion of particles:

$$k_{\mathrm{HC}} = k_{\mathrm{f}}\left[\frac{k_{\mathrm{p}} + (n-1)k_{\mathrm{f}} - (n-1)V_{\mathrm{p}}(k_{\mathrm{f}} - k_{\mathrm{p}})}{k_{\mathrm{p}} + (n-1)k_{\mathrm{f}} + V_{\mathrm{p}}(k_{\mathrm{f}} - k_{\mathrm{p}})}\right]. \tag{4}$$

Here, k_{HC} is the predicted thermal conductivity of the composite system, k_{f} is the conductivity of the liquid, k_{p} is the conductivity of solid particles, V_{p} is the particle volume fraction, and n is the empirical shape factor (for spheres $n = 3$). Other theoretical approaches yield essentially the same results within the limits of a small particle volume fraction.

For further analysis, it is convenient to introduce the excess-thermal-conductivity-enhancement coefficient κ, defined as

$$\kappa = \frac{k_{\mathrm{eff}} - k_{\mathrm{f}}}{k_{\mathrm{HC}} - k_{\mathrm{f}}}. \tag{5}$$

In the above definition, κ is simply the ratio of measured thermal conductivity increase divided by the increase predicted by the HC theory. Consequently, $\kappa = 1$ indicates agreement with the macroscopic theory, and $\kappa > 1$ measures the magnitude of thermal-conductivity enhancement.

A central result of the macroscopic approach based on the diffusive heat transport is that particle size does not play a role and only the particle shape and volume fraction affect thermal conductivity (see Eq. (4)). This is inconsistent with the above-mentioned experimental results, which clearly demonstrate that, for example, at the same volume fraction, k_{eff} is greater for 15 nm particles than for 40 nm particles. The effects of particle shape, however, have not been explored systematically.

Furthermore, according to the macroscopic theory, for a given volume fraction (assuming spherical particles for simplicity), the maximum conductivity is achieved when $k_{\mathrm{p}} \gg k_{\mathrm{f}}$ and is given by

$$k_{\mathrm{HC}} = k_{\mathrm{f}}\left(\frac{1 + 2V_{\mathrm{p}}}{1 - V_{\mathrm{p}}}\right), \tag{6}$$

which is the upper limit of the thermal transport enhancement within the macroscopic theory. Also, a closer examination of Eq. (4) shows that particles of $k_{\mathrm{p}} = 10k_{\mathrm{f}}$ or greater lead to an increase of k_{HC} close to the limiting value given by Eq. (6); surprisingly, any further increase of k_{p} has little effect on the thermal conductivity of the composite. Physically, this behavior arises because with significantly (10 times or more) higher particle thermal conductivity, the temperature across the particle becomes essentially constant, thereby providing the same boundary condition for the heat-flow equation in the surrounding liquid. Because the thermal conductivities of nearly all crystalline solids are at least ten times those of liquids, the above analysis would suggest that the thermal conductivity of nanofluids should be independent of particle composition; experimentally, this is clearly not the case. Moreover, the HC limit can be greatly exceeded, as exemplified by measurements of thermal conductivity in Cu nanofluids, in which $\kappa > 10$.

Finally, we note that the shape factor n (Eq. (4)) is >3 for nonspherical particles and therefore the thermal conductivity of a suspension of elongated particles can be enhanced. This shape factor is related to the ratio of the surface area of the particle to the surface area of a spherical particle with the same volume [7]. To account for a ten-fold larger increase in thermal conductivity, the required aspect ratio of elongated particles is on the order of 100 [7], and even a three-fold larger enhancement requires an aspect ratio of the order of 5. Such large aspect ratios seem unrealistic, because the nanoparticles used in the experiment are more or less spherical. It thus appears that the nonsphericity of grains can only be a small contribution to the measured excess thermal conductivity.

3. Potential mechanisms of enhanced heat conduction in nanofluids

Based on the above comparison with experimental results, one must conclude that the macroscopic theory of heat transport in composite materials fails for the case of nanofluids. In the following, we examine a comprehensive list of the factors that are potentially responsible for the inadequacy of the theory. First, we discuss the possibility that the enhancement of thermal conductivity arises from the Brownian motion of the particles. Second, we analyze how much of an increase in the thermal conductivity can be expected from molecular-level layering of the liquid at the liquid/particle interface. Third, we examine the nature of heat transport in nanoparticles and the validity of the key assumption of the macroscopic theory of diffusive propagation of heat in both particles and in the liquid matrix. Finally, we consider the effects of clustering of nanoparticles, both by forming direct solid–solid paths and by possible clustering effects mediated by liquid existing within the limit of a short interparticle distance. Our analyses will allow us to narrow the list of mechanisms capable of explaining the unusual enhancement of heat transport in nanofluids.

3.1. Brownian motion

Brownian motion, by which particles move through liquid and possibly collide, thereby enabling direct solid–solid transport of heat from one to another, can be expected to increase thermal conductivity. This is not, however, accounted for by the HC theory, which assumes a static composite material. Brownian motion is characterized by the particle diffusion constant D, given by the Stokes–Einstein formula

$$D = \frac{k_B T}{3\pi\eta d}, \tag{7}$$

where k_B is the Boltzmann constant, η is the fluid viscosity, and d is particle diameter.

With Eq. (7), one can estimate the effect of Brownian motion on the thermal conductivity by comparing the time scale of particle motion with that of heat diffusion in the liquid. Equivalently we can compare the time required for a particle to move by the distance equal to its size τ_D, given by

$$\tau_D = \frac{d^2}{6D} = \frac{3\pi\eta d^3}{6k_B T} \tag{8}$$

with time required for heat to move in the liquid by the same distance τ_H;

$$\tau_H = \frac{d^2}{6\chi} = \frac{d^2 c_p \rho}{6k_f}. \tag{9}$$

For water at room temperature ($\eta = 0.01$ g/cm s, $k_f = 0.4$ W/m K, $\rho = 1$ g/cm^3, $c_p = 4.2$ J/g) and with $d = 10$ nm, Eqs. (8) and (9) give $\tau_D \approx 2 \times 10^{-7}$ and $\tau_H \approx 4 \times 10^{-10}$ s, respectively. The ratio of τ_D/τ_H is $\approx$500 and decreases to $\approx$25 when the particle size is equal to the atomic size ($\approx$0.5), demonstrating that the thermal diffusion is much faster than Brownian diffusion, even within the limits of extremely small particles.

The above comparison demonstrates that the movement of nanoparticles due to Brownian motion is too slow to transport significant amounts of heat through a nanofluid, a conclusion supported by the results of MD simulations discussed in Section 4. However, Brownian motion could have an important indirect role in producing particle clustering, which, as we shall describe Sections 3.3 and 3.4, could significantly enhance thermal conductivity.

3.2. Liquid layering at liquid/particle interface

A large body of literature addresses the effect of the interfacial resistance in thermal conductivity that arises from the formation of a weak interfacial contact [15]. This could not be the origin of the discrepancy between theory and experiment in nanofluids, however, because this Kapitza resistance would lead to an overestimate of k by Eq. (4) and a decrease in thermal conductivity with decreasing grain size, contrary to the experimental results [5,6].

By contrast, an interface effect that could enhance thermal conductivity is the layering of the liquid at the solid interface [16], by which the atomic structure of the liquid layer is significantly more ordered than that of bulk liquid. Given that crystalline solids (which are obviously ordered) display much better thermal transport than liquids, such liquid layering at the interface would be expected to lead to a higher thermal conductivity.

To estimate an upper limit for this effect, let us assume that the thermal conductivity of this interfacial liquid is the same as that of the solid. The resultant larger effective volume of the particle-layered-liquid structure would enhance the thermal conductivity (See Fig. 1). Then, for example, to double the effective volume V_{eff} of a particle with $d = 10$ nm would require a layered-liquid thickness of $h \approx 2.5$ nm. However, experiments [17] and simulation [16] have shown a typical interfacial width that is only on the order of a few atomic distances, i.e., $\approx$1 nm. Thus, although the presence of an interfacial layer may play a role in heat transport, it is not likely to be solely responsible for the enhancement of thermal conductivity. This is particularly true for Cu nanofluids, where the experimentally observed increase in thermal conductivity is more than an order of magnitude larger than that predicted by the HC theory [8].

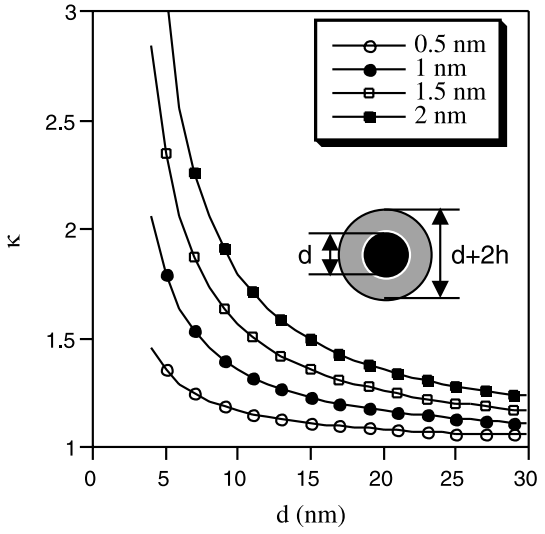

Fig. 1. Excess thermal-conductivity enhancement κ due to formation of highly conductive layered-liquid structure at liquid/particle interface for several values of layer thickness h as a function of particle diameter d.

3.3. Nature of heat transport in nanoparticles

Macroscopic theories assume diffusive heat transport (Eq. (1)). In crystalline solids, such as those used in nanofluids, heat is carried by phonons, i.e., by propagating lattice vibrations. Such phonons are created at random, propagate in random directions, are scattered by each other or by defects, and thus justify the macroscopic description of heat transport. In metals, the heat is primarily carried by electrons, which also exhibit diffusive motion at the microscopic level.

Within the simplest theory due to Debye, the mean free path l of a phonon is given by [18]

$$l = \frac{10aT_m}{\gamma T}, \tag{10}$$

where T_m is the melting point, a is the lattice constant ($\approx$0.5 nm), and γ is the Gruneisen parameter (of $\approx$1) [19]. For a typical nanoparticle, such as Al_2O_3, at room temperature $T_m/T \approx 7$ leading to $l \approx 35$ nm. Consequently, phonons cannot diffuse in the $\approx$10 nm particles but must move ballistically across the particle (see Fig. 2).

The above analysis demonstrates that the assumption of diffusive heat transport in nanoparticles is invalid; consequently, a macroscopic theory, such as the HC theory, does not apply and a theoretical treatment based on ballistic phonon transport is required [20]. However, from the macroscopic point of view, it is difficult to envision how ballistic phonon transport could be more effective than very-fast-diffusion phonon transport, particularly to the extent of explaining the order of magnitude larger increase of thermal conductivity in Cu nanofluids. For either ballistic or fast-diffusive phonon transport, the temperature within the solid particle will be essentially constant, providing the same boundary condition for heat flow in a low-thermal-conductivity liquid.

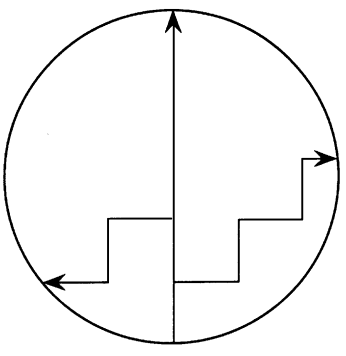

Fig. 2. Schematic diagram of ballistic and diffusive phonon transport mechanisms in a solid particle.

However, other ballistic phonon effects could lead to a significant increase in thermal conductivity. In particular, if the ballistic phonons initiated in one particle can persist in the liquid and reach a nearby particle, a major increase of thermal conductivity is expected. Because the phonon mean free path is much shorter in the liquid than in the particle, such an effect may only operate if the separation between particles is very small, likely on the order of the thickness of the layered liquid ($\approx$1–2 nm). As illustrated in Fig. 3, the particles in a nanofluid are surprisingly close together even at relatively low packing factions. For example, the surfaces of 10 nm particles are, on average, only separated by 5 nm at a 5% packing fraction. Moreover, because particles move constantly due to Brownian motion, locally, they may be much closer and thus enhance coherent phonon heat flow among the particles. Indeed, an analogous phenomenon was observed in experiments on sound propagation in colloidal systems, in which acoustic excitations propagated coherently between neighboring particles when the diameter of particles was comparable to the wavelength of the sound [21].

3.4. Effects of nanoparticle clustering

By creating paths of lower thermal resistance, clustering of particles into percolating patterns would have a major effect on the effective thermal conductivity. However, clustering to the extent that solid agglomerates span large distances are unlikely; moreover any such large clusters would most likely settle out of the fluid. Indeed, although the percolation threshold for random dispersions is $\approx$15% volume fraction in three

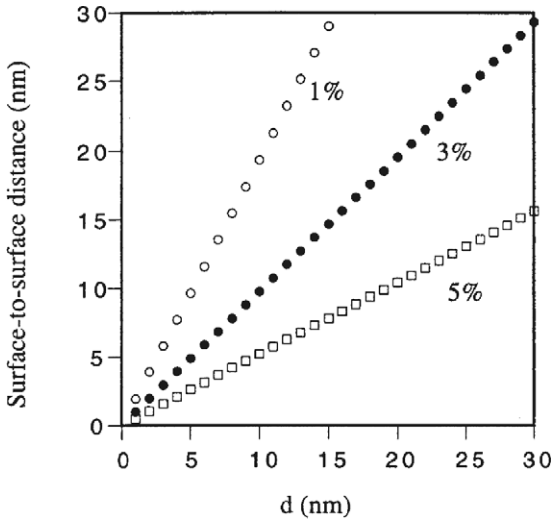

Fig. 3. Average surface-to-surface distance between particles for three particle volume fractions as a function of particle diameter d.

dimensions, the unusual enhancement of thermal conductivity is already observed at very low volume fractions of ≈1% and less.

Although percolating structures cannot be set up, local clustering is possible and indeed has been observed experimentally [4,8]. The effective volume of a cluster, i.e., the volume from which other clusters are excluded, can be much larger than the physical volume of the particles. Since within such clusters, heat can move very rapidly, the volume fraction of highly-conductive phase (V_p in Eq. (4)) is larger than the volume of solid and according to Eq. (4) may significantly increase thermal conductivity. The effect of clustering is illustrated in Fig. 4, which shows the excess thermal conductivity enhancement κ 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, which 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, as described in Section 3.3. 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.

We note, however, that in general 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.

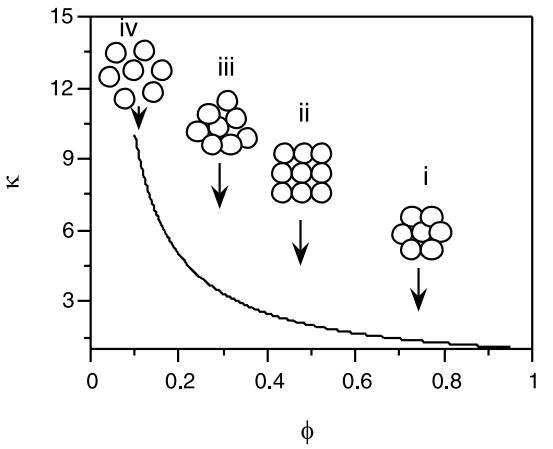

Fig. 4. Excess thermal conductivity enhancement κ due to increased effective volume ϕ of highly conducting clusters. Schematic diagrams indicate (from right to left) (i) closely packed fcc arrangement of particles, (ii) simple cubic arrangement, (iii) loosely packed irregular structure of particles in physical contact, and (iv) clusters of particles separated by liquid layers thin enough to allow for rapid heat flow among particles.

4. Molecular-level simulations

In the previous section, we used simple physical arguments to place upper limits on the possible effects that various mechanisms could have on enhancing thermal transport. To investigate the effects in more detail, a more sophisticated approach, such as molecular simulation, is required. To illustrate how molecular-level simulation is capable of shedding light on heat transport in nanofluids we present here results of our MD simulations that are related to the issues of Brownian motion and heat transport in the particles.

The methodology for studying thermal transport properties of liquids [22] and solids [23] by means of MD simulations is well established. The approach, based on calculations of heat and mass fluxes via molecular-level formulas, can be directly applied to a solid–liquid system such as a nanofluid.

Transport coefficients, such as the diffusion constant, viscosity, or thermal conductivity, can be computed from equilibrium simulations by using the Green–Kubo relationships [22] that are the consequences of the fluctuation–dissipation theorem. For example, the diffusion constant can be determined from the measurements of the mean-squared displacement of the diffusing particles. Such an approach to measuring transport coefficients is quite challenging experimentally but rather straightforward in molecular simulations, where positions and velocities of each atom, as well as the interatomic forces, are known precisely at all times.

The key in equilibrium molecular level simulations is to evaluate the heat flux, J_Q, which is given by the formula

$$J_Q = \sum_i (E_i^k + E_i^p - h_v)\mathbf{v}_i + \sum_i \sum_{j \neq i} \mathbf{r}_{ij}(\mathbf{F}_{ij}\mathbf{v}_j), \qquad (11)$$

where E_i^k and E_i^p are the kinetic and potential energy of atom i, respectively, h_v the averaged enthalpy, $\mathbf{v}_i$ the velocity vector of atom i, $\mathbf{r}_{ij}$ the vector connecting atoms i and j, $\mathbf{F}_{ij}$ the force acting on atom i due to interactions with atom j and $\mathbf{v}_j$ the velocity vector of atom j.

The first term in Eq. (11) represents convective transport of kinetic and potential energy with velocities v_i summed over all atoms. In this term "per

atom'' averaged enthalpies, h_v for the liquid and solid atoms are subtracted from the atomic energies, since this part of the energy does not contribute to heat flux. The second term is a double sum over all atoms and represents heat transfer via interatomic interactions (i.e., forces, $\mathbf{F}_{ij}$).

In equilibrium simulations, the heat flux J_Q fluctuates near zero, and, according to the Green–Kubo relationship, thermal conductivity can be calculated from the equation

$$k = \frac{1}{k_B T^2 V} \int_0^\infty \mathrm{d}t \langle J_Q(0) J_Q(t) \rangle, \tag{12}$$

where V is the volume and

$$\langle J_Q(0) J_Q(t) \rangle \tag{13}$$

is the time-averaged correlation between heat flux at time t_1 and $t_2 = t_1 + t$. The quantity given by Eq. (13) is called the heat-current autocorrelation function in as much as it involves correlation of the same quantity at various times [22].

According to Eq. (12), when the heat flux remains correlated with itself for a long time, the thermal conductivity is high. That is indeed the case in crystalline solids where propagating phonons provide long-lasting correlations. In liquids, such correlations are short lived, and thus lead to a relatively low thermal conductivity. In addition to allowing the calculation of the thermal conductivity, detailed analysis of the heat flux autocorrelation function $\langle J_Q(0) J_Q(t) \rangle$ provides insights into the transport mechanism, such as information on the correlation time.

For our molecular simulations, we use a simple model of the liquid and solid, both described by the Lennard–Jones (LJ) interatomic potential. The binding energy between the solid atoms ε_{ss} is chosen to be 10 times larger than that between the liquid atoms ε_{ll}. The fact that the melting point for the LJ potential is proportional to ε allows the study of stable solid–particle–liquid systems. Moreover, with such interatomic interactions, the macroscopic thermal conductivity of the crystalline solid is much higher than that of the liquid. Our choice of model system was motivated by the existence of an extensive literature on the thermal transport properties of both the LJ liquid [24] and solid [25], and by its computational efficiency. The results reported here were obtained from a model system that consisted of a single 2 nm-diameter spherical crystalline solid particle in a cubic unit cell with a linear dimension of 3.5 nm; i.e., at a 10% solid volume fraction.

To demonstrate the role of Brownian motion in thermal transport by direct molecular simulations, we compare the heat flux autocorrelation functions for two slightly different simulations of the same system. In the first simulation, all atoms were allowed to move according to Newton's equations of motion, whereas in the second simulation, the center of mass of the solid particle was constrained to a fixed position. According to Fig. 5, the heat flux autocorrelation functions for both simulations are essentially indistinguishable, demonstrating that not only the thermal conductivity (which is given by the integral of the autocorrelation function, Eq. (12)) but also the detailed microscopic mechanism of heat transport is not affected by Brownian motion. This result is in full accord with the ''back of the envelope'' calculations presented in Section 3.1.

To elucidate 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 shown in Fig. 6. 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.

The above results clearly demonstrate that inside solid particles, heat moves in a ballistic manner that involves multiple scattering from the solid/liquid

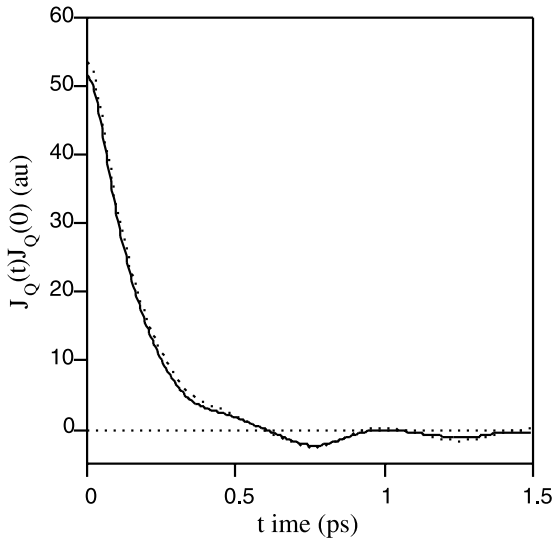

Fig. 5. Heat current J_Q autocorrelation function obtained by MD simulations of 2 nm particle at 10% volume fraction, with (——) and without (……) constrained center of mass. The near equality of results demonstrates the very small effect of Brownian motion on thermal transport.

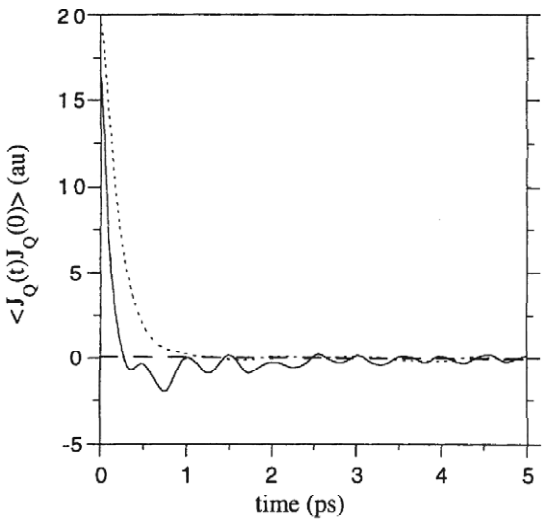

Fig. 6. Heat current autocorrelation functions for liquid (– – – –) and particle (——), showing monotonic decay of correlations in liquid and oscillatory decay in solid, a signature of ballistic phonons moving back and forth inside the particle.

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 get reflected back into the particle, thereby not contributing to macroscopic heat transport.

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

5. Discussion and outlook

In this paper, we have taken the first steps to developing a fundamental understanding of heat transport in solid nanoparticle colloids under stationary conditions. Most important, we have evaluated the extent to which four specific mechanisms could contribute to the thermal conductivity. Although these are the four most obvious mechanisms (to us), we cannot exclude the possibility that others may be important also. While the role Brownian motion appears not to be important, an understanding of the effects of other proposed mechanisms (layering at the solid/liquid interface, ballistic phonon transport, and clustering) require further experimental and simulation studies.

Experimentally, the key requirement is the separation of the various effects on thermal transport. For example, introducing a surfactant into the fluid, thereby preventing particle agglomeration, may elucidate the role of "direct-contact" clustering. To see if the increase of macroscopic thermal conductivity of particles beyond 10–50 times over the value of fluid conductivity matters, contrary to the predictions of macroscopic theory, a comparison of a pure metal and metal with impurities (thus characterized by much lower macroscopic conductivity) would be illuminating. Effects of ballistic heat transport within the particle can be addressed by comparing conductivity of crystalline-particle nanofluids with amorphous-particle nanofluids, which are characterized by a very short phonon mean-free path, rendering a ballistic mechanism inoperable.

It will also be important to characterize the distribution of particles in the fluid by scattering techniques with $\approx$10 nm resolution. Such a characterization would allow us to determine not only the average distance between particles, but also to determine a complete distribution function of particle separations. A complete distribution function will be the key in evaluating the enhancement of thermal conductivity that arises from coherent heat transport between particles separated by thin liquid layers ("liquid-mediated" clustering). To allow systematic investigations of particle size effects on the discussed heat transport mechanisms, all of the above studies should be performed at particle sizes that are well defined and at particle-size distributions that are as narrow as possible.

Modeling in general and molecular simulations in particular can complement experimental work to provide information that is very difficult if not impossible to obtain experimentally. For example, the role of the particle/liquid interface can by studied systematically by varying the strength of the interactions between solid and liquid atoms. The analysis of interfacial effects can also be carried out for a planar geometry under a temperature gradient, thus allowing for plane-by-plane analysis of heat transport in the solid and at the solid/liquid interface [26] as a function of surface-to-surface separation between two solid regions. Also, the effects of well-defined particle nanoclusters (spherical or elongated, densely packed or loosely packed) can be studied directly by molecular simulations.

The synergy within such an integrated experimental-simulation approach can be used to guide the development of nanofluids with maximized heat transfer. The benefits of such optimized nanofluids can be truly outstanding. For example, in a typical cooling system, pumping power must be increased by a factor of 12 to improve heat transfer by a factor of 2, i.e., if a nanofluid

could double the rate of heat transfer, the required pumping power could be cut by an order of magnitude. Such an accomplishment could lead to a major technological breakthrough in the development of a new class of energy-efficient heat transfer fluids for many applications, including waste reduction, waste utilization, transportation, and manufacturing.

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