Probing Transport Mechanisms in Nanofluids by Molecular Dynamics Simulations

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Abstract

Enhanced thermal conduction in nanofluids is an observed phenomenon for which the underlying mechanistic processes are still being debated. We perform molecular dynamics (MD) simulations of the time-dependent heat current correlation to obtain the systematic, dynamical details at the atomistic level. Using a model system of Xe base fluid and Pt nanoparticles, we obtain the enhancement effects which show qualitatively the same variation with the concentration as the experiments. Our study, which is work in progress, indicate that the interatomic interactions between fluid and the nanoparticle, which can be much stronger than the interaction between fluid particles, as well as nanoparticle interactions, are significant factors in understanding the heat transport mechanisms of nanofluids.

Key Words: nanofluids, thermal conductivity, interatomic potential, molecular dynamics.

1. Modeling Efforts in Nanofluids

Nanofluid connotes a colloidal suspension with dispersed nano-size particles. Experiments over the past decade have revealed that thermal conductivity of the suspension can be significantly higher than that of the base medium [1-4]. Early attempts to explain this behavior have made use of the classical model of Maxwell for statistically homogenous, isotropic composite materials with randomly dispersed spherical particles of uniform size [1]. This model is generally applicable to dilute suspensions with micron size particles. With sub-micron sized oxide particles, Maxwell's model predicts a noticeably lower thermal conductivity enhancement and in the case of very fine metallic (Cu and Au) nano-particles, the enhancement is too low by almost an order of magnitude [2,3].

Keblinski *et al* [4] have examined four possible mechanisms for the anomalous enhancement observed in nanofluids. The first is the transport of thermal energy by Brownian motion of the nano-particles. An order-of-magnitude calculation shows that the Brownian effects are not strong enough to explain the observed anomaly. A similar conclusion was also reached by Wang and Xu [1] with a somewhat different set of assumptions, and also later confirmed by a molecular dynamics (MD) simulation [4]. On the other hand, recent reports continue to attribute the enhanced conductivity to Brownian motion of the nano-particles [5, 6, 7]. We will return to this issue below.

Another mechanism, the formation of liquid layers around the particles, is considered by Keblinski *et al* [4]. The basic idea is that liquid molecules can form layers around the solid particles, thereby enhancing the local ordering. Since phonon transfer in crystalline solid is very effective, such local ordering in the liquid can lead to enhanced heat transport. A recent MD simulation by Xue *et al* [8] confirmed the presence of short-ranged ordering of liquid molecules, but surprisingly observed little or no effect on the thermal conductivity.

The third mechanism is related to the nature of heat transport in nano-particles. It is pointed out [4] that the generally accepted diffusive transport mechanism is not valid at the nano-scale, instead ballistic transport is more realistic. If ballistic 'phonons' initiated in one particle can persist in the liquid and get transmitted to another solid particle, the heat transport can significantly increase. The phonon mean free path in the liquid is typically small because local ordering is limited to few atomic diameters. Since, particles are constantly moving by Brownian motion, there is a possibility that somewhat coherent phonon transfer is possible even with low particle concentrations. An order-of-magnitude analysis by Prasher *et al* [7] shows that even fast crystalline-like phonon modes account only for a fraction of the thermal conductivity increase observed in the experiments.

Lastly, Keblinski *et al* [4] explore the possibility of nano-particles forming clusters and their effects on the thermal conductivity. This type of model may be appropriate if the particles are in the form of nanotubes or if they are not finely dispersed [9].

In contrast to the assessments of Keblinski *et al* [4] and Wang and Xu [1], Jang and Choi [5], Kumar *et al* [6] and Prasher *et al* [7] hypothesized that Brownian motion of the nano-particles plays a leading role in energy transport of in nanofluids. While these models agree on the overall mechanism, they differ appreciably in how Brownian motion affects the thermal conductivity of the nanofluid. For instance, the models do not have a consistently defined Brownian velocity. Kumar *et al* [6] defines the Brownian velocity as

$$u_B = \frac{2k_B T}{\pi \mu d_p^{\,2}} \tag{1}$$

Prasher *et al* [7] defines it differently as

$$u_B = \sqrt{\frac{18k_B T}{\pi \rho_p d_p^{\,3}}} \tag{2}$$

Still another form is used by Xuan *et al* [10]

$$u_B = \sqrt{\frac{2k_B T}{3\pi \mu d_p}} \tag{3}$$

Eqn. (3) arises from the solution of the Langevin equation, while Eqn (2) is taken from the kinetic theory. Eqn. (1) appears to have its origin in the Langevin description, but temperature and particle size dependence seems to be arbitrary. Brownian velocity is not a formal concept in Langevin dynamics, as the solution to the Langevin equation gives an expression only for the velocity auto-correlation and the mean square displacement. As a result, the models differ significantly in their predictions of the thermal conductivity. Eqn. (2) is successful for oxides which have comparatively low thermal conductivities. Eqn. (1) predicts a substantially higher Brownian velocity and it fits well with the data for gold nanofluids.

Besides the different expressions for the Brownian velocity there are other dissimilarities among the Brownian models. Both Jang and Choi [5] and Prasher *et al* [7] employ the concept of 'micro' convection where flow fields akin to those around macroscopic structures are assumed around the nano-particles. This precludes the use of these models for extremely small nano-particles. Furthermore, non-dimensional parameters such as Reynolds number (*Re*) are defined differently in each model. Prasher *et al* [7] defines a *Re* that is inversely proportional to the square root of particle diameter, while Jang and Choi [5] adopted a definition that turns out to be independent of particle diameter.

To investigate the anomalous behavior in the nanofluids, we consider an approach that involves explicitly the inter-atomic interactions between the nano-particles and the fluid atoms. We will study a model system consisting of a base fluid and nanoparticles of varying concentrations. Using the Green-Kubo formalism in linear response theory, we will systematically determine the thermal conductivity of the base fluid and the nanofluid. Although this approach has been used successfully to study transport processes in single components fluids and solids, its applicability to binary systems is not in question. On the other hand, the simulation results are physically meaningful only if the interaction potentials used can be considered to be sufficiently realistic. For our study we have developed a base fluid model of xenon and a nanofluid model of platinum particles in xenon. We obtain thermal conductivity results where the enhancement effect is about an order of magnitude greater than that given by the Maxwell's model, findings which are qualitatively consistent with the experimental data on metallic particles in more complex base fluids. We also find the enhancement effect is dependent on the strength of the inter-atomic potentials, which suggests that the transport processes are strongly coupled to the nature of chemical binding that exist between the particles in a nanofluid.

2. Molecular Dynamics (MD) Simulations

Molecular dynamics simulation has been successfully employed in the past to predict the thermal conductivity of solids [11,12] and fluids [13,14]. Through linear response theory one can obtain the transport coefficients by using simulation to calculate appropriate time correlation functions. Besides the inter-atomic potentials for all the atoms in the system, no further assumptions are needed to study the dynamical processes that occur in the nanofluid at any temperature, density, and nanoparticle concentration. From a conceptual standpoint, this approach can provide atomic-level details that are useful for elucidating the intrinsic transport mechanisms that operate in the model system.

The thermal conductivity is obtained as a time integral of the microscopic heat flux correlation given by [15]

$$k = \frac{V}{3k_B T^2}\int_0^\infty \left\langle \mathbf{J}(t)\bullet\mathbf{J}(0)\right\rangle dt \qquad (4)$$

where **J** denotes the microscopic heat flux

$$\mathbf{J} = \frac{1}{V}\left[\sum_j \frac{1}{2} e_j \mathbf{v}_j + \frac{1}{2}\sum_{i\neq j}(\mathbf{r}_{ij} : \mathbf{F}_{ij})\bullet\mathbf{v}_j)\right] \qquad (5)$$

e_j is the instantaneous excess energy of atom j,

$$e_j = \sum_j \frac{1}{2} m_j \mathbf{v}_j{}^2 + \frac{1}{2}\sum_{i\neq j}\varphi_{ij} \qquad (6)$$

$\mathbf{F}_{ij}$ is the pair-wise force acting on each atom and is given by the (negative) of the gradient of the potential. Further mechanistic insight is possible through the behavior of the time-dependent correlation function. For example, in solids the correlation function shows a two stage relaxation, an initial rapid decay associated with the local (single particle) dynamics followed by a slower component associated with phonon dynamics. This is in contrast to liquids where generally one sees only a single relaxation associated with diffusive transport such as the Brownian motion.

The determination (or selection) of realistic interatomic potentials is the foremost challenge to any molecular dynamics simulation where the aim of the study is to obtain the physical properties that can be compared with actual measurements. For simple systems such as rare-gas liquids and solids there exist potential models which are quite accurate and yet sufficiently tractable for simulations that require significant number of particles and extended simulation periods. Thus the Lennard-Jones model gives reasonably accurate thermodynamic and transport properties of argon, krypton and xenon, which conceivably can serve as the base fluid. If the base fluid is to be water, empirical potentials also exist, but now one has to incorporate the charged species (protons and oxygens) in the simulation which makes the interpretation of results significantly more involved. Nanofluids experiments thus far have involved metallic or ceramic particles, for which some potentials are available but thermal conductivity studies largely have not been attempted. In view of this situation and given that our intention is to study generic behavior rather than a specific physical system, we have decided to investigate a model nanofluid with xenon as the base fluid and platinum as the nanoparticle. A major reason for this choice is to take advantage of the available data on Pt-Xe [16], Pt-Pt [17], and Xe-Xe [18], which we have used to construct the equivalent Lennard-Jones potentials, as shown in Fig. 1. One can see quite clearly that the Pt-Xe potential depth is much greater than the potential depth for the base fluid. Therefore it may not be too surprising that the presence of platinum, even at low concentrations, can have a significant effect on the heat transport.

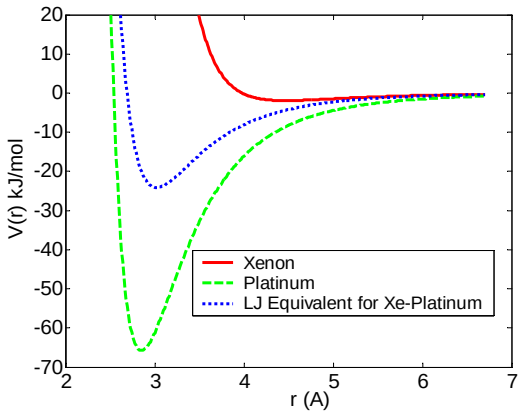

Fig. 1. Comparison of Lennard-Jones potential for Pt-Pt, Pt-Xe and Xe-Xe interactions.

Our MD simulations are performed in the NVT ensemble with periodic boundary conditions and velocity rescaling. Results on the xenon base fluid are obtained at a temperature of 246 K and a pressure of 119 MPa, the system being in the liquid state. In simulating a nanofluid we replace a fraction of the xenon atoms by well dispersed platinum atoms. This is an idealization which allows the xenon fluid to have the maximum interaction with the platinum

atoms; it also completely ignores all finite size effects of the nanoparticles.

4. Results

We first validate our simulation methodology and the interatomic potential by comparing thermal conductivity and viscosity results for argon with experimental data. Fig. 2 shows the behavior of the heat flux correlation function. The monotonic decrease is typical of liquids; as mentioned before, the thermal conductivity is just the area under this curve.

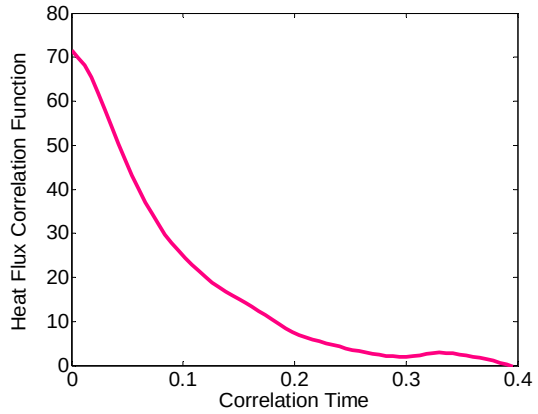

Fig. 2. Heat Flux correlation function for Argon T^*=1.06, ρ^*=0.821.

Table 1. Comparison of transport properties evaluated with MD with NIST data

T^*=1.06 P^*=0.821	NIST P = 82 MPa	MD P = 82 MPa	Δ
κ (W/m-K)	0.135	0.141	4.4 %
μ (μPa-s)	226.3	219.9	2.8 %

Table 1 gives the comparison with NIST data [19], including a similar determination of the viscosity by evaluating the stress correlation function, at 127 K and 82 MPa. This demonstrates that MD simulation is capable of predicting the transport properties of fluids with good accuracy.

Next we consider the effects of the dispersed platinum atoms on the thermal conductivity of our model nanofluid. Effectively each platinum atom represents a "nanoparticle" which interacts with other platinum atoms, along with all the xenon atoms, according to the potentials shown in Fig. 1. The thermal conductivity thus obtained, expressed as percent enhancement relative to the conductivity of liquid xenon, is shown in Fig. 3. Also given are the predictions of Maxwell's model.

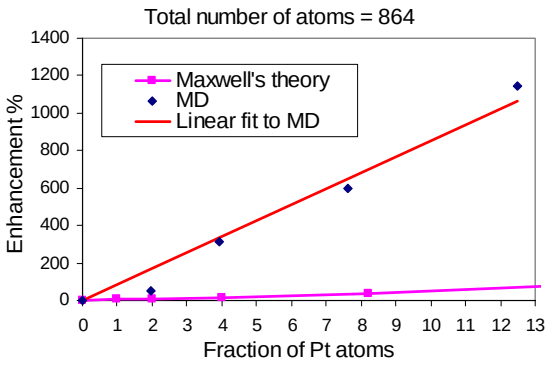

Fig. 3. Enhancement in thermal conductivity as a fraction of platinum atoms.

One sees an essentially linear increase in the thermal conductivity with the fraction of platinum atoms. The magnitude of the enhancement is considerably larger than predicted on the basis of Maxwell's model. These features are qualitatively consistent with what has been observed in the nanofluids, as indicated by a comparison of our Xe-Pt model results with experimental data on copper-ethylene glycol system [20] in Fig. 4. In view of the differences between our model and the actual nanofluid, especially the absence of long-range charged interactions in the former, it is premature to ascribe any further significance at this stage.

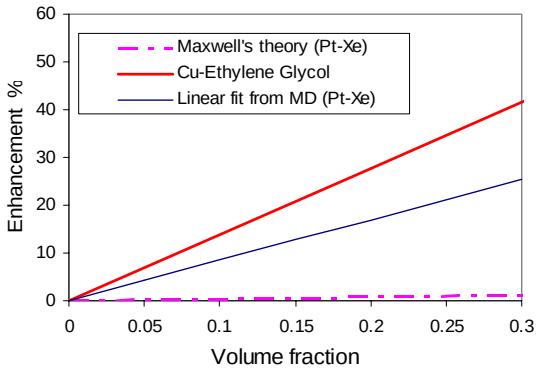

Fig. 4. Comparison of enhancement with Xe-Pt with reported data from Cu-ethylene glycol [20].

When the "nanoparticles" are inserted into the liquid, we see interesting changes in the heat flux correlation curves (see Fig. 5). With increasing number fraction, the correlation increases in strength which results in an increase in thermal conductivity. At higher number fractions, the correlation function shows a distinct oscillatory behavior. This oscillation clearly indicates the presence of a dynamical mode involving interactions among the platinum atoms. It remains to be clarified what is the nature of this mode. If we regard the Fourier transform of the heat flux correlation as a dynamic conductivity, then the conventional thermal conductivity is the zero-frequency component or the static value. In this context, an oscillatory correlation function would signify a resonant or collective process. Oscillations in the heat flux correlation are known to occur in crystalline and amorphous states [11].

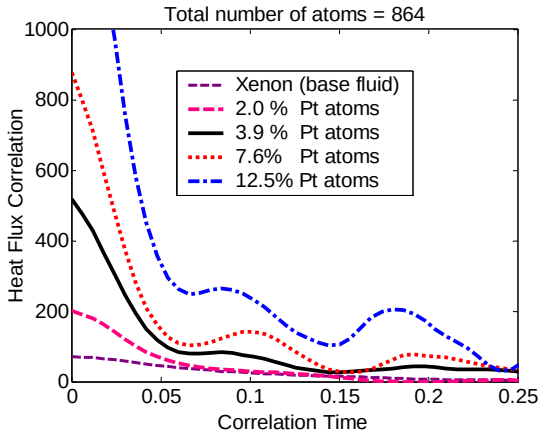

Fig. 5. Heat flux correlation functions for different Pt atom fractions.

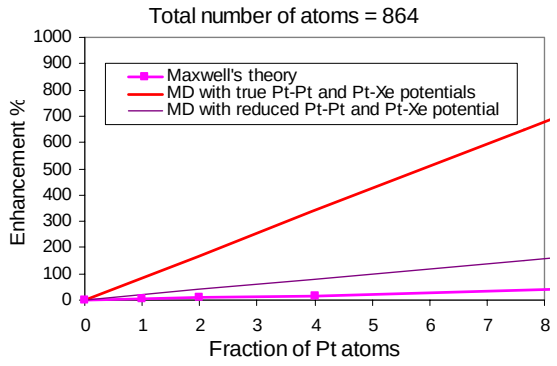

Fig. 6. Enhancement in thermal conductivity with Pt-Pt and Pt-Xe potentials reduced by a factor of 2.

To probe the effects of inter-particle interactions further, we have repeated a simulation in which we decrease the Pt-Xe and Pt-Pt potential depth to half its original value. Not surprisingly, we observe a decreased enhancement which is shown in Fig. 6. Our results suggest that the thermal conductivity of a nanofluid may be strongly coupled to the inter-atomic interactions between the constituent atoms of the nanofluid.

4. Summary

Nanofluid connotes a colloidal suspension with dispersed nano-sized particles. Experiments in the past decade reveal that the thermal conductivity of the suspension is significantly higher than that of the base medium. This enhancement is many times higher than what is classically predicted by the Maxwell's model. Recently, there have been several attempts to correlate this anomaly with the Brownian motion of the nano-particles. These models appear to be only partially successful; at present no single description is able to explain the existing experimental data.

In this work, we focus on the inter-atomic interactions between the nano-particles and the fluid atoms. We study a model nanofluid system of liquid xenon and dispersed platinum atoms through molecular dynamics simulations. Using the Green-Kubo formalism in linear response theory, we calculate the thermal conductivity of base fluid (Xe) and the nanofluid (Xe+Pt). We observe that that the thermal conductivity of the nanofluid, is higher than that of the base fluid and also many times higher than what is predicted by the Maxwell's model (see Fig. 3). The enhancement effect is of the same order of magnitude as observed in experiments using metallic particles. When the depth of the inter-atomic potential is reduced, the enhancement effect decreases correspondingly, thus indicating a direct coupling between thermal conductivity and the inter-atomic potential.

There is more information from the MD simulations than what we have extracted thus far. We are in the process of analyzing the time-dependent heat flux correlation function in greater detail. We are hopeful that by systematically combining this information with other properties of the nanofluid model (available from the same simulations) such as the various radial distribution functions, velocity autocorrelation functions, and mean-square displacements, a deeper understanding of the mechanisms underlying the transport behavior of nanofluids can be obtained.

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Nomenclature

u_B	Brownian velocity
k_B	Boltzmann constant
d_p	Diameter of nano-particle
T	Temperature
k	Thermal conductivity
e	Excess energy
V	Volume
J	Heat flux correlation function
F	Force
r	Position vector
v	Velocity
μ	Viscosity
ρ	Density
φ	Potential energy
*	Reduced MD units

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