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A proof for insignificant effect of Brownian motion-induced micro-convection on thermal conductivity of nanofluids by utilizing molecular dynamics simulations

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It has been recently demonstrated through experiments that the observed high enhancements in thermal conductivity of nanofluids are due to aggregation of nanoparticles rather than the previously stated mechanism of the Brownian motion-induced micro-convection. In this paper, we use equilibrium molecular dynamics simulations to investigate the role of micro-convection on the thermal conductivity of well-dispersed nanofluids. We show that while the individual terms in the heat current autocorrelation function associated with nanoparticle diffusion achieve significant values, these terms essentially cancel each other if correctly defined average enthalpy expressions are subtracted. Otherwise, erroneous thermal conductivity enhancements will be predicted, which are attributed to Brownian motion-induced micro-convection. Consequently, micro-convection does not contribute noticeably to the thermal conductivity and the predicted thermal conductivity enhancements are consistent with the effective medium theory. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4791705>]

INTRODUCTION

The thermal conductivity enhancement brought about by suspending nanoparticles in a fluid has been a highly debated topic for more than a decade. Two main mechanisms of thermal conductivity enhancement have been reported, i.e., aggregation of nanoparticles into clusters and the Brownian motion-induced micro-convection. The argument by the first group^{1–9} of researchers, who believe that clustering is the mechanism explaining the high thermal conductivity enhancement of nanofluids, is that in well-dispersed nanofluids, the thermal conductivity enhancement just follows the effective medium theories for well-dispersed mixtures of spherical nanoparticles. Greater thermal conductivity enhancements are then explained by the aggregation of nanoparticles creating high aspect-ratio particles or networks of conductive particles. In both cases, the effective medium theory based simply on conduction explains the observed behavior.⁵ The other group of researchers has identified the Brownian motion of nanoparticles as the origin of the observed anomalous thermal conductivity enhancement. Early studies, such as those by Kumar *et al.*¹⁰ and Bhattacharya *et al.*,¹¹ have pointed to the direct influence of the Brownian motion on thermal conductivity. Later on, convection introduced by the Brownian motion of either a single nanoparticle or multiple nanoparticles was identified as the major mechanism of thermal conductivity enhancement in nanofluids.^{12–16} Due to the temperature and particle size dependence of the Brownian motion, many researchers have studied the variation of thermal conductivity with the particle size and temperature.^{10,12,13}

In particular relevance to this investigation, some researchers performed equilibrium molecular dynamics (EMD) simulations and reported significant contributions of

“micro-convection” to thermal transport,¹⁶ or claimed that “convection” of the interfacial (particle-fluid) interaction energy contributes significantly to thermal conductivity.¹⁷ On the other hand, direct method simulations, where a heat source and sink are introduced to create a heat flux and the associated temperature gradient,¹⁸ demonstrated thermal conductivity enhancements perfectly consistent with the effective medium theory predictions indicating that micro-convection plays no role. In this study, we address the above-discussed discrepancy in great detail, emphasizing issues that arise when EMD simulation is used for determining thermal conductivity of nanofluid multi-component systems. Different contributing components to thermal conductivity obtained via EMD simulations are evaluated and the terms that can lead to erroneous high thermal conductivities are identified. Furthermore, it is proven that, for well-dispersed nanofluid systems, these high-value micro-convection-induced components of the thermal conductivity cancel each other. In effect, the shortcoming of a number of previous EMD simulations that report anomalous high values of thermal conductivity is highlighted.

SIMULATION METHODOLOGY

Thermal conductivity can be determined from EMD simulations via the Green-Kubo relationship,

$$k_{ii} = \frac{1}{Vk_B T^2} \int_0^\infty \langle J_i(t) J_i(0) \rangle dt, \quad i = x, y \text{ or } z. \quad (1)$$

In Eq. (1), k_{ij} is the ij -th component of the thermal conductivity tensor at temperature, T . Quantity V is the volume of the simulation cell and k_B is the Boltzmann constant. The time integral is over the heat current autocorrelation function

(HCACF) that is obtained from EMD simulations and the symbol $\langle \rangle$ indicates ensemble averaging. The molecular formula for the heat current, $\mathbf{J}(t)$, for a two-component system is given by

$$\mathbf{J}(t) = \overbrace{\left[\sum_{j=1}^N \mathbf{v}_j E_j - \sum_{\alpha=1}^2 h_{\alpha} \sum_{j=1}^{N_{\alpha}} \mathbf{v}_{\alpha j} \right]}^{\text{Convective}} + \overbrace{\left[\frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \mathbf{r}_{ij} (\mathbf{v}_j \cdot \mathbf{F}_{ij}) \right]}^{\text{Virial}}, \quad (2)$$

where \mathbf{v}_j and E_j are the velocity and energy (sum of the potential and kinetic energies) of particle j , respectively. Quantities \mathbf{r}_{ij} and \mathbf{F}_{ij} are the displacement vector and the force between particles i and j , respectively. Quantity N is the total number of particles and N_{α} is the number of particles for species α , whereas h_{α} denotes the average partial enthalpy of species α . In Eq. (2), the first group of terms represents the convective current and the second group is identified as the heat current due to the particle-particle interactions. Subtracting of the correct average enthalpy term is extremely important since such quantity just moves silently with diffusing particles, but the associated energy is not exchanged and does not contribute to heat conduction. Interestingly, when a single-component system is simulated in equilibrium and at overall zero total momentum, the average enthalpy subtraction is irrelevant as the sum of the velocities is equal to zero ($\sum_{j=1}^{N_{\alpha}} \mathbf{v}_{\alpha j} = 0$).

For each of the species, the average enthalpy is defined as

$$h_{\alpha} = \frac{\sum_{i=1}^{N_{\alpha}} \left[K_i + P_i + \frac{1}{3} \left(m_i v_i^2 + \frac{1}{2} \sum_{j=1}^N \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right) \right]}{N_{\alpha}}, \quad (3)$$

where K_i and P_i are the time-averaged kinetic and potential energies of particles of species α , respectively. The first two terms are the kinetic (K_i) and potential (P_i) energies that constitute the internal energy (E_i) and the third term is the PV term, which includes kinetic and interaction (virial) terms. In our recent study,¹⁹ we provided extensive validation of the partial enthalpy formula by determining the thermal conductivity of various two-component systems, including gas, liquid, and solid mixtures.

ANALYSIS METHODOLOGY

As presented in Eq. (2), the heat flux can be divided into two main components: convective and virial (interaction) terms. Correspondingly, HCACF will have four terms resulting from multiplying each one of these two terms by the other. Therefore, we formally decompose the expression for the HCACF into the four terms,

$$HCACF = \langle CC \rangle + \langle CV \rangle + \langle VC \rangle + \langle VV \rangle. \quad (4)$$

In Eq. (4), for example, $\langle CC \rangle$ stands for the autocorrelation function of the convective heat current and $\langle CV \rangle$ is the cross-correlation function of the convective and virial currents.

For further analysis, we will decompose the convective term into the energy and average enthalpy terms as follows:

$$C = \frac{1}{V} \left[\sum_{j=1}^N \mathbf{v}_j E_j - \sum_{\alpha=1}^2 h_{\alpha} \sum_{j=1}^{N_{\alpha}} \mathbf{v}_{\alpha j} \right] = E - H. \quad (5)$$

The associated terms in the HCACF are EE , HH , EH , and HE . For the average energy or average enthalpy, the autocorrelation function is determined by the autocorrelation function of the average velocity, i.e.,

$$\mathbf{v}(t) = \frac{1}{N} \sum_{j=1}^N \mathbf{v}_j. \quad (6)$$

The velocity autocorrelation function has the dimension of the mass diffusion coefficient and can be defined as the diffusion constant

$$D = \int_0^{\infty} \langle v_i(t) v_i(0) \rangle dt, \quad i = x, y \text{ or } z. \quad (7)$$

We will use the above-described characterizing methodology to analyze the results of the EMD simulations in relation to the dominance of the various contributions to thermal conductivity.

MODEL

The nanofluid system was formed by carving a sphere within methane atoms and placing copper atoms on an FCC crystal sites with a lattice constant of 3.61 Å. The Lennard-Jones (LJ) potential was chosen for intermolecular interactions among all pairs of particles. The LJ parameters (σ and ϵ) for copper atoms are 2.34 Å and 9.4512 kcal/mol, respectively.²⁰ For methane molecules, the optimized potentials for liquid simulations (OPLS) united-atom force field was used.²¹ In this force field, CH₄ is taken as a single interaction site for LJ interactions. The LJ parameters (σ and ϵ) for methane united atoms are 3.73 Å and 0.294 kcal/mol, respectively. The Lorentz-Berthelot mixing rule²² was used for determining the LJ parameters between methane pseudo atoms and copper atoms.

Simulations were carried out on systems with two different temperatures of 100 K and 110 K and two different copper particle diameters of 12.703 Å and 25.406 Å. For the cases of $T = 110$ K and $d = 12.703$ Å, a nanoparticle containing 87 copper atoms was suspended in different number of methane molecules leading to five different volume percentages of 0.15% (10957 methane molecules), 0.23% (6893 methane molecules), 0.35% (4612 methane molecules), 0.47% (3410 methane molecules), and 0.66% (2438 methane molecules). For the cases of $T = 100$ K and $d = 12.703$ Å, a nanoparticle containing 87 copper atoms was suspended in different number of methane molecules giving rise to three different volume percentages of 0.36% (4612 methane molecules), 0.49% (3410 methane molecules), and 0.69% (2438 methane molecules). For the cases of $T = 110$ K and $d = 25.406$ Å, a nanoparticle containing 683 copper atoms was suspended in different number of methane molecules

leading to three different volume percentages of 0.55% (23 187 methane molecules), 0.86% (14 754 methane molecules), and 1.06% (12 054 methane molecules).

The Velocity Verlet algorithm was used to integrate the Newton's equation of motion numerically with a time step of 1 fs. Systems were initially equilibrated for 200 000 time steps under isothermal-isobaric condition (NPT) with $T=100$ K or 110 K (depending on the case) and atmospheric pressure and further equilibrated under constant volume and energy condition (NVE) for 200 000 time steps. Finally, the process was followed with 1 000 000 time steps under the NVE condition and the fluctuating heat current was monitored every 5 fs. For each case, the HCACF curves were obtained by averaging over 8 different simulations having different initial velocity distributions. All simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics package.²³

RESULTS

In Fig. 1(a), the variation of the MD-predicted values of the ratio of the thermal conductivity of nanofluid and the thermal conductivity of base fluid (k/k_f) as a function of the particle volume percentage is shown for two temperatures of 100 K and 110 K and two particle diameters of 12.703 Å and 25.406 Å. The EMD-predicted values for all cases are close to the Maxwell model for prediction of thermal conductivity of well-dispersed suspensions of spherical particles.

To gain further insight into a potential role of the convective term, we also show the contributions of the CC , VV , and CV (which due to time reversal symmetry is equal to VC) terms in Fig. 1. In all cases, by far, the major term in thermal conductivity of the nanofluid is the virial contribution (k_{vv}). The predicted values for this term do not vary with volume percentage. The remaining three terms involving convection, including the cross terms (k_{cv} and k_{vc}) and the k_{cc} term are small by comparison to the k_{vv} term. The k_{cc} term, which is directly associated with the Brownian motion-related micro-convection, increases slightly with volume percentage, but is much smaller than the virial term. These results clearly demonstrate that the thermal conductivity of a nanofluid is dominated by the atom-atom interaction mechanism rather than the diffusion/micro-convection terms.

In Fig. 2, we show the contributions to thermal conductivity due to the EE and HH terms for the case of 12.703 Å nanoparticle at 0.35% volume percentage and 110 K. These cancelling contributions that have been overlooked by some previous studies are more than one order of magnitude greater than the total conductivity value. However, as shown in the bottom panel of Fig. 2, both EE and HH terms essentially follow a behavior of the integral over time of the velocity autocorrelation function. This means that the EE term is dominated by the constant value of the average energy. As a consequence, the $EE + HH$ terms essentially cancel the $HE + EH$ terms. This result indicates that it is extremely important to subtract the correctly defined average enthalpies in

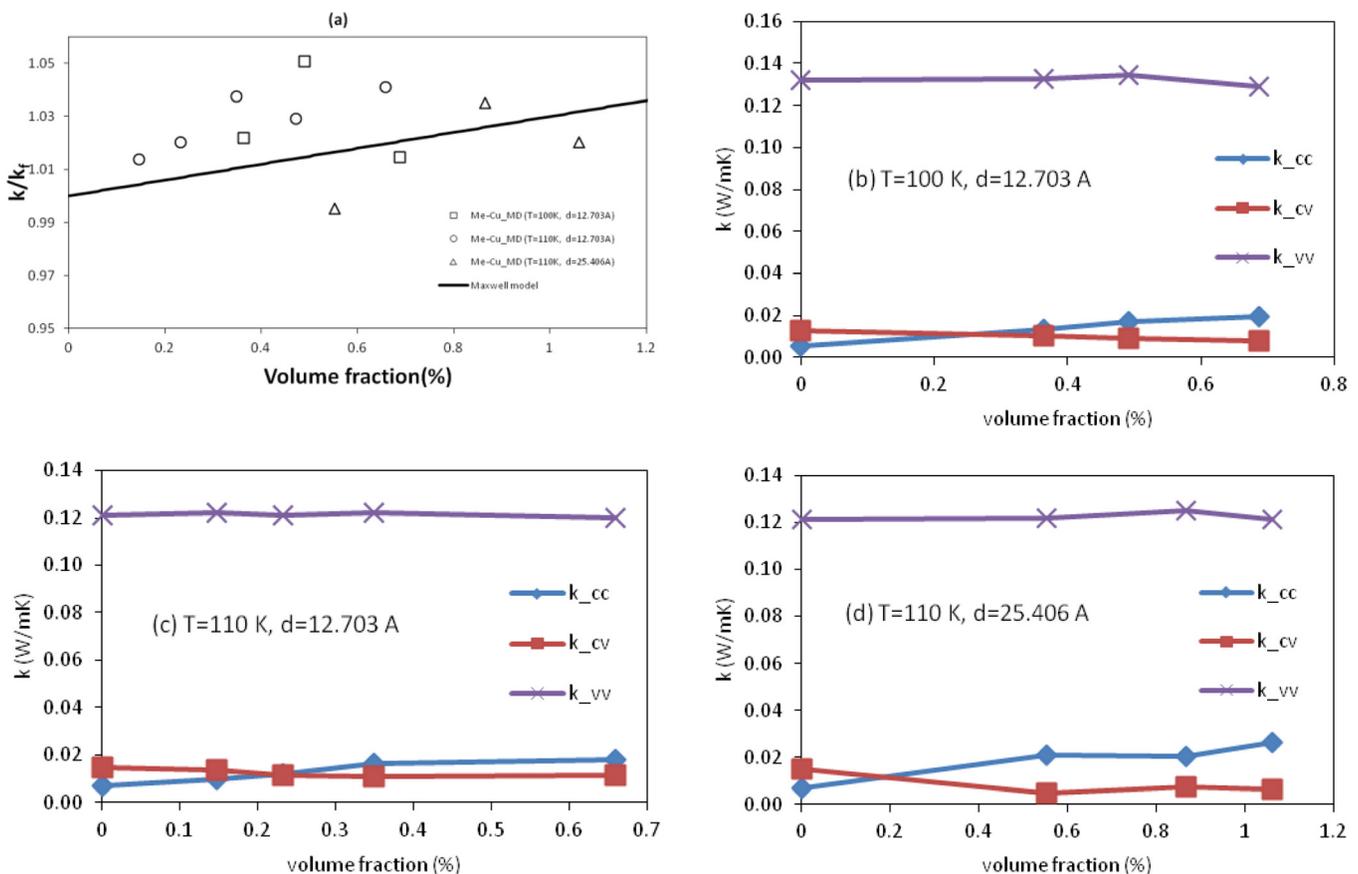


FIG. 1. Contributions of various terms to the thermal conductivity as a function of particle volume percentages for various temperatures and particle sizes.

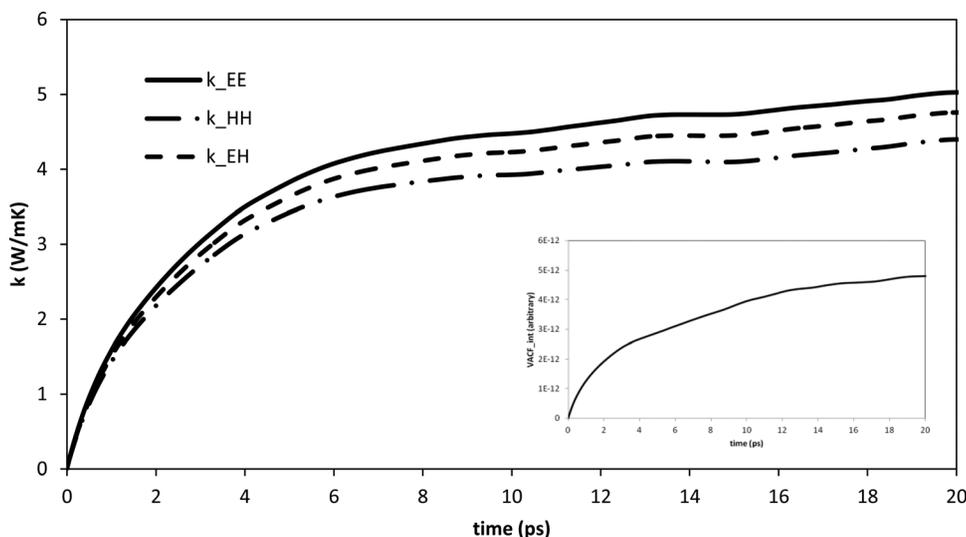


FIG. 2. Time integrals of the correlation functions associated with the convective term contributions to the thermal conductivity for a nanofluid with 12.703 Å nanoparticle at 0.35% volume percentage and 110 K. The inset shows time integral of the center of mass velocity autocorrelation function.

the heat current expression. Otherwise, the cancellation will not occur, leading to significant and erroneous contributions to thermal conductivity on behalf of the Brownian motion.

In complementing the above clarifications set forth in this paper, the self-diffusion coefficient of the nanoparticle at $T=110\text{K}$ with $d=12.703\text{Å}$ is plotted versus the volume percentage in Fig. 3. The diffusion coefficient rises with the particle volume percentage, which is due to the increasing magnitude of the velocity of the center of mass. Correspondingly, the EE and HH terms that have resulted from multiplying the energy and velocity terms follow the same trend, i.e., strong direct dependence on the volume percentage. However as discussed above, these terms will cancel out with the EH and HE terms and will have no significant effect on thermal conductivity.

SUMMARY AND CONCLUSIONS

We used equilibrium molecular dynamics simulations to determine the role of micro-convection on thermal transport in nanofluids. We showed that while individual convective terms in the heat current expression are significant, they essentially cancel each other, leading to the conclusion that

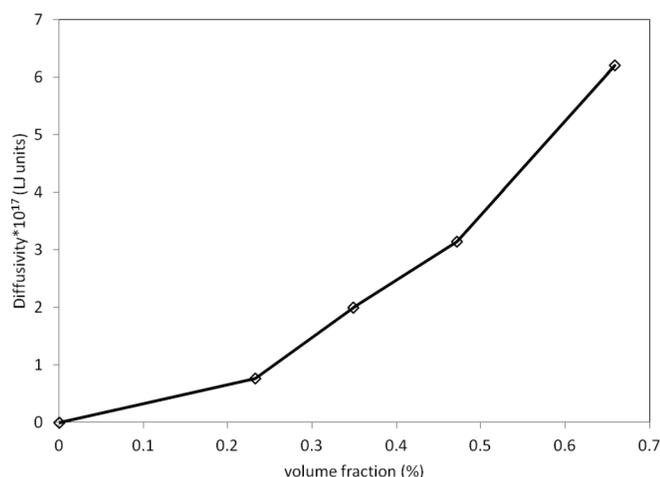


FIG. 3. Self-diffusion coefficient of the nanoparticle as a function of volume percentage.

micro-convection has a minor role in thermal transport of nanofluids. We demonstrated that the critical technical issue in EMD thermal conductivity determination is the subtraction of the correct value of the average enthalpy of each species from the energy in the convective term of the heat current.

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