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Molecular dynamics study of the thermal conductivity in nanofluids

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ABSTRACT

We evaluate the thermal conductivity of a model nanofluid at various volume fractions of nanoparticles with equilibrium (EMD) and non-equilibrium (NEMD) molecular dynamics simulations. The Green-Kubo formalism is used for the EMD simulations while a net heat flux is imposed on the system for the NEMD simulations. The nanoparticle-nanoparticle, fluid-fluid and fluid-nanoparticle interactions are all taken as Lennard-Jones potentials. An empirical parameter is added to the attractive part of the potential to control the hydrophilicity of the nanoparticles, hence controlling how well dispersed are the nanoparticles in the base fluid. The results show that the aggregation of the nanoparticles does not have a measurable effect on the conductivity of the nanofluid. Nanofluids with volume fractions of 2% and 3% show an enhanced conductivity with respect to the bulk fluid. Surprisingly, nanofluids with higher volume fractions did not show any enhancement of the conductivity.

1. Introduction

Nanofluids are defined as a base fluid containing well dispersed nano-sized solid particles [1]. Recent experiments have suggested that nanofluids tend to have higher thermal conductivity than the base bulk fluids [2]. There are few numerical studies of the thermal conductivity of nanofluids in the literature, one of the most prominent work was performed by Sarkar et al. [3] They modelled a copper nanoparticle in liquid argon using equilibrium molecular dynamics simulations (EMD). The Lennard-Jones potential was used to model both the fluid and the nanoparticle. They evaluated the thermal conductivity of the nanofluid for a single copper nanoparticle and varying volume fraction. The results suggest that the increase in thermal conductivity is mostly due to the increased mobility of fluid atoms.

Sankar et al. studied water-platinum nanoparticles nanofluid with EMD [4]. They used four different interactions to have a more realistic nanofluid. They observed that the thermal conductivity of the nanofluid increases proportionally with the temperature and volume fraction of the nanoparticle. Ghosh et al. calculated the thermal conductivity of water-copper nanofluids using a hybrid MD-stochastic model [5], they also observed a linear increase with the volume fraction. Additionally, Mohebbi et al. [6] and Cui et al. [7] also reported an increase in thermal conductivity of nanofluids with the volume fraction of nanoparticles. On the other hand, some studies observed that the rate of enhancement decreases with the volume fractions of nanoparticles, leading in some cases to a plateau at a relatively small volume fractions of 2% to 5% [3,8,9].

Cui et al. observed that the thermal conductivity of nanofluids decreases as the nanoparticle diameter increases [10,11]. However, depending on the type of nanoparticles increasing size can also lead to increasing thermal conductivity [13]. Another factor influencing the thermal conductivity is the shape of the nanoparticles [1]. Indeed, it was observed that higher surface to volume ratio of nanoparticles leads to a larger enhancement of the thermal conductivity [11]. Cui et al. suggested that the shape of the nanoparticles has an impact on the radial distribution function leading in turn to changes on the thermophysical properties of the nanofluid [12].

Nanoparticle clustering is one of the mechanisms proposed for the enhancement of thermal conductivity [14]. Kang et al. studied nanoparticle aggregation with two nanoparticles and observed that the thermal conductivity increases when the nanoparticles are close together [15]. Similarly, Lee et al. observed the aggregation of nanoparticles results in a higher increase of the thermal conductivity compared to well dispersed nanoparticles [16]. On the other hand, Sedighi et al. studied the thermal conductivity of a water-silicon dioxide nanofluid and observed well dispersed nanofluids had a slightly larger enhancement of the thermal conductivity with respect to aggregated nanoparticles [9].

Xue et al. studied the effect of layering on the thermal conductivity for a simple liquid with non-equilibrium molecular dynamics simulations (NEMD) [17]. They did not observed any difference between the thermal conductivity of the layered liquid and the bulk liquid and suggested to rule out layering as a mechanism for the enhancement of thermal conductivity in nanofluids. Keblinski et al. suggested that Maxwell's theory of well dispersed particles should be given up and allowed chain-forming morphologies for nanoparticles so that the disagreement between the experiment and the effective medium theory could be clarified [18]. They mentioned the importance of aggregation

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on the thermal transport enhancement.

Babaei et al. calculated thermal conductivity of different multi-component systems via the Green-Kubo formula using EMD by comparing the results with the NEMD calculated results [19]. They did not observe any significant enhancement for well-dispersed nanofluid. They underlined the importance in correctly defining the average energies used in the evaluation of the heat current.

In this study, we use a generic coarse-grained model for the nanoparticles and a Lennard-Jones fluid for the base fluid. The interactions strengths are varied in order to evaluate the effect of layering and aggregation on the thermal conductivity. The volume fraction is also varied. The thermal conductivity is first evaluated with EMD then validated with NEMD simulations.

The paper is organized as follows: In Section 2, we outline the details of model we use in the study. Then, in Section 3, we compute the thermal conductivity for varying aggregations and volume fractions of nanoparticles. Finally conclusions are drawn in Section 4.

2. Model

We are interested in studying the universal properties of a nanofluid, consequently we use a coarse grained model. The base fluid is modeled as a Lennard-Jones fluid, hence, the fluid-fluid interactions are described by a 6–12 Lennard-Jones potential [20],

$$\mathscr{V}_{\mathrm{LJ}}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & \text{for } r < r_c \\ 0 & \text{for } r > r_c \end{cases} \tag{1}$$

where the cut-off distance is taken as $r_c = 2.5\sigma$. We note that the same value is used for all the interactions in the model.

The nanoparticles are modelled as roughly spherical molecules with a radius of $r = 2\sigma$. They consist of 58 atoms. The atoms inside nanoparticles interact with the Lennard-Jones potential of Eq. (1), and additionally, with the Finitely Extensible Non-Linear Elastic (FENE) potential [21],

$$\mathscr{V}_{\mathrm{FENE}}(r) = \begin{cases} \frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] & \text{for } r < R_0 \\ \infty & \text{for } r \geqslant R_0 \end{cases} \tag{2}$$

where $R_0 = 1.5\sigma$, $k = 30\,\epsilon/\sigma^2$. The nanoparticles are first constructed and equilibrated in a separate molecular dynamics simulation, and afterwards are added to the bulk fluid. The bulk fluid and nanoparticles are mixed to obtain 4 simulation boxes with varying nanoparticle volume fractions of 2%, 3%, 6% and 10%. We define the volume fraction of the nanoparticles φ as,

$$\varphi = \frac{\frac{4}{3}\pi r_p^3}{V} \tag{3}$$

where r_p is the radius of the nanoparticle and V is the volume of the simulation box. The nanoparticles interact with the fluid and with other nanoparticles through a modified Lennard-Jones potential,

$$\mathscr{V}_{\alpha\beta}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \zeta_{\alpha\beta}\left(\frac{\sigma}{r}\right)^{6}\right] & \text{for } r < r_c \\ 0 & \text{for } r > r_c \end{cases} \tag{4}$$

where $\alpha, \beta = n, f$ denotes the interaction occurs between a nanoparticle atom (n) or a fluid atom (f). The coefficient $\zeta_{\alpha\beta}$ controls the magnitude of the attractive part of the interaction, large $\zeta_{\alpha\beta}$ corresponds to a hydrophilic interaction. In order to have a nanofluid we have to prevent the nanoparticles from flocculating, and thus have a well dispersed fluid. Consequently, the interaction between nanoparticles should be hydrophobic. We found that $\zeta_{nn} = 0.3$ ensures the nanoparticles are well dispersed in the fluid, and fixed its value in all simulations. On the other hand, ζ_{nf} permits to investigate how the thermal conductivity is influenced by the hydrophilicity of the nanoparticles, and as a consequence of the density of the base fluid in their vicinity. For this purpose, we use three different values of the hydrophilicity parameter of the fluid-nanoparticle interaction, namely $\zeta_{nf} = 0.5$, $\zeta_{nf} = 1$ and $\zeta_{nf} = 1.5$.

Initially, a total number of 5000 fluid atoms are arranged in a regular FCC lattice. The system size in the x and y directions is 15σ and varies between $29-31.5\sigma$ in the z direction in order to reach the same fluid density. The equations of motion are then integrated with the Velocity Verlet algorithm with a time step of $\Delta t = 0.001\tau$. The molecular dynamic code and the post-processing codes are all written in FORTRAN 90. The code is parallelized with the openMP protocol and each simulation was performed with 4 processors. The total energy E and the total momentum P are computed to check the validity of the code since they are both conserved quantities. Using the Lennard-Jones phase diagram from literature [22], we choose a phase point corresponding to a liquid state. The temperature and density are taken respectively as $k_B T = 1.1\,\epsilon$ and $\rho = 0.7798\sigma^{-3}$.

For four different nanofluid models and three different Lennard-Jones potential, in total 12 sets, we initially run 10^7 time steps to equilibrate the system, indeed it is known that in order to evaluate the transport properties of nanofluids a stable dispersion should be achieved [23]. The resulting coordinates are then used for all the simulations. We depict in Fig. 1 snapshots of nanofluids consisting of 6 nanoparticles. The left-hand-side corresponds to $\zeta_{nf} = 1.5$, a well dispersed nanofluid whilst the right-hand-side has $\zeta_{nf} = 0.5$ which yields an aggregated nanofluid.

In order to check the consistency of our results we compute the thermal conductivity coefficient with two different methods. First with equilibrium molecular dynamic simulation thanks to the Green-Kubo relation [24],

$$\lambda = \frac{V}{3k_B T^2}\int_0^\infty d\tau \langle \mathbf{j}_\lambda(\tau)\mathbf{j}_\lambda(0)\rangle, \tag{5}$$

where T is the temperature of the system, V is the volume, k_B the Boltzmann constant and $\mathbf{j}_\lambda$ the microscopic heat current which is given by [14],

$$\mathbf{j}_\lambda = \frac{1}{V}\left[\sum_{i=1}^{N} \mathbf{v}_i(E_i - \langle E_i\rangle) + \frac{1}{2}\sum_{i<j}^{N} \mathbf{r}_{ij}[\mathbf{F}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j)]\right] \tag{6}$$

where E_i is the instantaneous energy of the i^{th} atom,

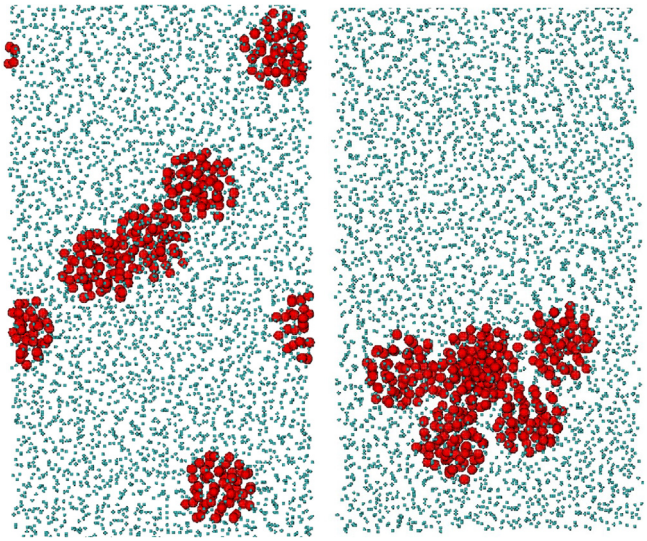

Fig. 1. Two equilibrated nanofluids with nanoparticle volume fraction of %10, on the left-hand-side $\zeta_{nf} = 1.5$ and on the right-hand-side $\zeta_{nf} = 0.5$.