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Determination of thermal conductivity of interfacial layer in nanofluids by equilibrium molecular dynamics simulation

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ABSTRACT

In this article, equilibrium molecular dynamics are performed to investigate the thickness and thermal conductivity of interfacial layer around the nanoparticle in dilute nanofluids. A nanofluids system of a 1-nm-diameter copper spherical nanoparticle immersing into argon base liquids and then a flat interface formed by liquid argon on the solid copper surface are studied. Green-Kubo formula is developed to calculate thermal conductivity of interfacial layer. Besides, the effect of solid-liquid interaction is studied. The nano-scale thin interfacial layer with more ordered structure and higher thermal conductivity than that of the base fluids is observed. Then the simulation results are incorporated into the modified Maxwell equation to calculate the effective thermal conductivity of nanofluids. The results indicate that the contribution of interfacial layer to thermal conductivity enhancement of nanofluids can be neglected.

1. Introduction

Nanofluids, formed by adding nanoscale-solid-particles into base fluids, has been put forward by Choi et al. [1] in 1995. Nanofluids have shown a huge application potential to be the next generation heat transfer fluids because of the superior thermal conductivity and acceptable suspension stability. Especially, some researchers found that the nanofluids at very low particles volume percentage showed anomalous enhancement in thermal conductivity as reviewed by Wang et al. [2] and Fan et al. [3]. For example, Eastman et al. achieved 40% increase in thermal conductivity for only 0.3% volume percentage copper nanoparticles dispersed in ethylene glycol [4]. These reported increases in thermal conductivity are much greater than the predictions by the conventional models basically derived from Fourier's law [5–7]. This demonstrates the fundamental limits of conventional models. Therefore, novel mechanism is necessary to be proposed to understand the heat transfer in nanofluids. The physical concepts of interfacial layer has been proposed by Choi et al. for the understanding of the anomalous thermal conductivity enhancement in nanotube suspensions [8]. Then the models for predicting effective thermal conductivity of nanofluids considering interfacial layer has been developed [9–13]. It has been well accepted that the thickness and thermal conductivity of the interfacial layer are two important parameters to verify the various models developed, which is, however, very difficult to be experimentally measured with the existing instruments. Thus some researchers tried to get the two parameters by theoretical arithmetic and postulation values as reviewed by Kotia et al. [14].

On the other hand, molecular dynamics (MD) simulation has been regarded as an effective approach to studying the heat conduction mechanism of nanofluids from the microscale level. MD has been widely used to simulate and investigate the thermophysical properties of nanofluids over the last decade. With this method, the study mainly concentrated on the various influential effects including the volume fraction of nanoparticles, temperature, Brownian motion of nanoparticles and the size and shape of nanoparticles in terms of the thermal conductivity as well as viscosity as reviewed by Jabbari et al. [15]. Among these studies, the structure and thickness of the interfacial layer surrounding nanoparticles has also been observed by the radial distribution function (RDF) or atom number density distribution to explain the improved heat transfer characteristic [17,21]. Nevertheless, only very few MD simulations have been done to calculate directly the thermal conductivity of interfacial layer which is another parameter as essential as the thickness [16–18]. The result of NEMD simulations for Au-Ar system by Liang et al. showed that the thermal conductivity of a 1-nm-thick interfacial layer is 1.6 times higher than that of the base fluids [17]. As shortly reviewed above, the study on the thermal conductivity of interfacial layer is scarce so far although it is a very important parameter for the establishment of new models for predicting thermal conductivity

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of nanofluids when the influence of the interfacial layer has to be considered.

In MD simulations, the thermal conductivity is generally calculated by the non-equilibrium molecular dynamics (NEMD) based on the Fourier's law also named direct method and the equilibrium molecular dynamics (EMD) based on the Green-Kubo theory. The Green-Kubo theory is more prevalent and superior than the direct method due to its smaller size effect and available full thermal conductivity tensor. Since the Green-Kubo formalism assumes that the spatial variation of an applied current must be equivalent to the spatial variation of the temperature gradient, thus computed thermal conductivity is limited to that for the homogenous system. However, Babaei et al. performed both EMD and NEMD simulations to determine the thermal conductivity of multi-component systems [16]. The results showed that the proper definition of the heat current in EMD simulations will lead to the consistency between the two methods. Thus the Green-Kubo theory is applied widely to calculating thermal conductivity of nanofluids by many researchers [18-20]. Especially, Sun et al. [21,22] attempts firstly to calculate effective thermal conductivity of nanofluids imposing in shearing fluids based on Green-Kubo formulism and the simulation results prove the feasibility of this way.

The above reviews indicate that Green-Kubo formulism based on the linear response theory has a well potential expansion capacity. Therefore in this paper the Green-Kubo formulism is developed to evaluate the magnitude of thermal conductivity of interfacial layer by modifying the definition of microscopic heat current and choosing suitable integral time. To our knowledge, it's the first attempt to calculate thermal conductivity of a part of system instead of the whole system by Green-Kubo formulism. In our work the number density distribution around nanoparticle is used to prove the existing of the interfacial layer and determine roughly its thickness. Thermal conductivity distribution is then used to determine precisely the thickness and thermal conductivity of the interfacial layer. Then the two parameters are incorporated into the Modified Mawell model [9] to investigate the contribution from interfacial layer to thermal conductivity enhancement of nanofluids. The work is expected to be of value from methodological and engineering point of view.

2. Model

Molecular dynamics simulation describes the atomic dynamics based on the Newtonian equations of motion. In general the original positions and velocities of a set of atoms are given according to the physical conditions of studied system (such as, density, temperature) and the required forces between atoms are evaluated by empirical or semi-empirical interatomic potentials (such as, Lennard-Jones [23], Stillinger-Weber [24], Tersoff [25]). Although the density functional theory can get analytical interatomic potentials, its calculations demand too many orders of magnitude than evaluated interatomic potentials to drive MD simulations. Then an integration scheme and time step are required to solve the Newtonian equations of motion to evolve the positions and velocities. Finally the time histories of the positions and velocities are recorded and analyzed.

In our work, atom argon and copper are chosen to form the base fluids and nanoparticles, respectively, which is widely used and accepted by many researchers [16–19,26,27] in the study field of nanofluids. Furthermore the mature potential function of argon is concise but very accurate, which is vital to the computation of liquid argon interfacial layer. All simulations are performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics package [28].

Potential functions $E(r_{ij})$ as the standard 12/6 Lennard-Jones [29] are chosen for the intermolecular interactions of argon-argon, copper-copper, and copper-argon, given by:

$$E(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \quad r_{ij} < r_c$$
$$E(r_{ij}) = 0 \qquad\qquad r_{ij} \geqslant r_c \tag{1}$$

where r_{ij} is the distance between two atoms i and j, ε the interaction strength, σ the atom length scale and r_c the cutoff radius (in this work r_c is chosen as 0.85 nm for all the intermolecular interactions). For the argon-argon interaction, ε and σ are chosen as $1.6540190 \times 10^{-30}$ g∗nm^2/fs^2 and 0.3405 nm, as well as for the copper–copper interaction, ε and σ $6.5581445 \times 10^{-29}$ g∗nm^2/fs^2 and 0.2338 nm [30], respectively. For the copper-argon interaction, ε and σ are generally estimated by Lorentz-Berthelot rules [31], given by:

$$\varepsilon_{Cu-Ar} = k\sqrt{\varepsilon_{Cu}\varepsilon_{Ar}}$$
$$\sigma_{Cu-Ar} = \frac{\sigma_{Cu} + \sigma_{Ar}}{2} \tag{2}$$

In our work, k is chosen as 0.5, 1.0 and 1.5, to simulate the weaker, usual and stronger solid-liquid interaction, respectively. The Lorentz-Berthelot rules are the most well-known mixing rules. It's noted that the mixing rules are only successful when the pair atoms have the same form of potentials function.

For the equilibrium molecular dynamics simulation thermal conductivity (λ) in Green-Kubo [30] form can be expressed as:

$$\lambda = \frac{V}{k_B T^2}\int_0^t < \boldsymbol{J}(t)\boldsymbol{J}(0) > dt \tag{3}$$

where k_B is Boltzmann constant. V and T are volume and temperature of the calculated region, respectively. < > denotes the average over different time origins. <$\boldsymbol{J}(t)\boldsymbol{J}(0)$> term is the heat current autocorrelation function (HCACF).

$\boldsymbol{J}$ is microscopic heat current, given by:

$$\boldsymbol{J} = \frac{1}{V}\left[\sum_i e_i \boldsymbol{v_i} - \sum_i S_i \boldsymbol{v_i}\right] \tag{4}$$

where e_i is the total energy of potential and kinetic of atom i. S_i is stress tensor, calculated as:

$$S = -\sum_i (\boldsymbol{f_{ij}}\boldsymbol{v_j})\boldsymbol{x_{ij}} \tag{5}$$

where $\boldsymbol{f_{ij}}$ is the force on i atom resulting from pairwise, bond, angle, improper, K space and internal constraint force interaction thanks to j atom. For our simulations only the pairwise interaction contributes to the force. $\boldsymbol{X_{ij}}$ is displacement vector from i to j atom.

Since the simulation is performed for discrete MD time steps, Eq. (3) for the calculation of thermal conductivity can be written as below form:

$$\lambda(t_M) = \lambda(M\Delta t) = \frac{\Delta t}{3k_B V T^2}\sum_{m=1}^{M}\frac{1}{N-m}\sum_{n=1}^{N-m}(\boldsymbol{J}(m+n)\boldsymbol{J}(n)) \tag{6}$$

where N is the number of MD time steps after equilibration, M is the number of integration time steps, and $\boldsymbol{J}(m+n)$ is the heat current at MD time step m + n. Theoretically, integration time steps M required infinite long to achieve high statistical accuracy, which is impossible for the practical simulations on computer. Besides the total simulation time steps N should be at least 10 times longer than integral time. Thus how to choose a suitable integration time steps M is critical to the precision and efficiency of calculated results. It will be discussed in the Section 3.1 in details.

It's worth noting that for our simulations the Green-Kubo formulism is extended to calculate thermal conductivity of a part of