On the temperature effect of nanofluid thermal conductivity by molecular dynamics simulation

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Nanofluids are a new class of nanotechnology-based heat transfer fluids that possess extraordinarily high thermal conductivity and flow stability. However, the deep mechanism for the strengthened conduction heat transfer in nanofluids has not yet been fully disclosed. This study investigated the thermal conductivities of water-based nanofluids by molecular dynamics simulations and examined possible reasons for the thermal conductivity enhancement from microscopic view. By establishing water-based nanofluids simulation models with copper nanoparticles installed, the simulations were performed under different temperature conditions. It was found that the thermal conductivity is a monotonic increasing function of thermodynamic temperature. By adding 1nm copper nanoparticle, the thermal conductivity of nanofluids is increased by more than 30%. By tracking the evolution of simulation system, it was concluded that multiple factors may be responsible for the conduction heat transfer enhancement in nanofluids. Fast heat transferring through the water molecules absorbed to the nanoparticles surface, as well as micro convection effect caused by the intense motions of nanoparticles are the most likely mechanisms.

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1. Introduction

Adding solid particles into fluid is a classical method to improve the thermal conductivity of single phase fluid [1]. As the thermal conductivity of solid material is hundreds of times larger than liquid, the thermal conductivity of solid particles suspension is larger than that of single phase liquid. However, if the average size of solid particles is in the millimeter or micrometer range, the high density solid particles easily precipitate in base fluid and cause pipe blockage or equipment abrasion, and therefore the application of this enhanced heat transfer method is restricted. Nano-material science flourishes since 1990. Some researchers introduced nano-materials into heat transfer and proposed the concept of nanofluids [2]. The term "nanofluids" refers to the homogeneous suspensions by adding a small quantity of nano-sized metallic or non-metallic particles into conventional heat transfer medium, such as water, ethylene glycol, or engine oil, etc. In recent years, researchers have verified that adding nanoparticles could significantly improve the conduction heat transfer in nanofluids and enhance heat transfer process [3-5]. Experiments also have found that nanoparticles are easy to steadily suspend in base fluid due to their small scale, and therefore nanofluids avoid problems of pipe blockage or equipment abrasion. In recent years, the poor thermal conductivity of conventional heat transfer medium has become a choke point for the further development of heat transfer and cooling technology. Take the advantage of features that nanofluids possessed, it is able to alleviate the restriction from working medium and develop a new generation of heat exchange equipment. And therefore nanofluids have drawn extensive attention due to their broad application prospects.

Studies on the thermal conductivity of nanofluids began in 1993. Masuda and his colleagues from Tohoku University in Japan added γ-$A1_2O_3$ of 13nm and TiO_2 of 27nm with a volume ratio of 4.3% into water and found that adding nanoparticles can significantly increase the effective thermal conductivity of fluid. Choi and his group from U.S. Argonne National Laboratory made a series of experimental studies on nanofluids [2,3,7]. Their valuable works revealed that thermal conductivity of nanofluids is influenced by many factors including bulk material of nanoparticle, nanoparticle size, volume concentration, and temperature, etc. Recent years, researchers have performed a number of experimental studies on nanofluid thermal conductivity measurement [8-16]. The results of previous experiments show that the effective thermal conductivity of the fluid increases when particle size decreases or the volume fraction increases. Experimental results on the influence of temperature show that the nanofluid thermal conductivity increases with increasing temperature. As it is hard and expensive to get smaller nanoparticles, the nanoparticles added in those experiments are generally

larger than 10nm. Although large nanoparticles can also significantly increase the thermal conductivity of base fluid, but adding smaller nanoparticles may get better results. However, there still lacks systematic study on the effect of adding nanoparticles that are smaller than 10nm.

The basic principle of Molecular Dynamics (MD) method is to solve Newton's motion equation of a simulation system composed of molecules or atoms, which is controlled by given potential functions and extra constraints. The microscopic process of the simulation system with time evolution is simulated, and meanwhile balance parameters and transport properties are calculated by statistical method. MD simulation is an effective and reliable approach to investigate thermal conductivity of nanofluids. By using MD method, Sankar [17] calculated thermal conductivity of platinum-water nanofluid based on Green-Kubo formula, and analyzed the influence of temperature and volume fraction for the thermal conductivity of nanofluids. Li [18] calculated the thermal conductivity of copper-argon nanofluids by using equilibrium molecular dynamics method, studied the effect of liquid adsorbed layer at the nanoparticle surface, and analyzed the impact of adsorption layer on the thermal conductivity of nanofluids. However, there still needs more research work on nanofluids by MD simulations.

In this study, we use MD simulation to calculate thermal conductivities of copper-water nanofluids at different temperatures, and analyze the change law of thermal conductivity with temperature. The simulation results are compared to experimental results to find the influence law. Furthermore, possible reasons for explaining the conduction heat transfer enhancement in nanofluids are investigated.

2. Methodology

2.1 Simulation method

MD method relates the thermal conductivity of fluid to equilibrium heat flow autocorrelation function through Green-Kubo equation [17], which is written as:

$$k = (1/V3k_BT^2)\int_0^\infty \langle J(t)\cdot J(0)\rangle dt \tag{1}$$

where k is thermal conductivity of fluid, k_B is Boltzmann's constant, T is thermodynamics temperature, V is volume, J is instantaneous microscopic heat flux vector, $<J(t)\cdot J(0)>$ is the heat flow autocorrelation function, and angular brackets denote taking oveall average. Heat flow vector can be calculated by:

$$J = (1/V)\left[\sum_j (1/2)e_j v_j + (1/2)\sum_{i\neq j}(r_{ij} : F_{ij})\cdot v_j\right] \tag{2}$$

where F_{ij} represents the interaction between atom i and atom j, which is ruled by interaction potential. And e_j represents surplus energy of the atom j, which is calculated by:

$$e_j = \sum_j (1/2)m_j v_j^{\,2} + (1/2)\sum_{i\neq j}\Phi_{ij} \tag{3}$$

Adopting suitable potentials is a critical step to ensure accuracy of the MD simulation results [17]. Generally, MD simulations employ empirical or semi-empirical potentials to describe interactions between atoms. Lennard-Jones (L-J) is a commonly used potential, which is used for describing interactions between gaseous or liquid atoms, which is written as:

$$u_{ij} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{4}$$

where r_{ij} represents the distance between atom i and atom j (r_{ij}=r_j-r_i), ε is characteristics potential energy of interactions between molecules, σ is characteristics diameter of molecule. The first item represents the repulsive force caused by overlap of the inner electrons or ions in an atom, and the second item represents the electrostatic attraction between dipoles.

During the MD simulation, resultant force on each atom meets the Newton's law [18]:

$$m_i \frac{d^2 r_i}{dt^2} = \sum_{j\neq i} F_{ij} \tag{5}$$

where m_i and r_i represent the quality and location of atom i, and the interaction between atom i and atom j can be written as:

$$F_{ij} = -\frac{\partial u_{ij}}{\partial r_{ij}} \tag{6}$$

Substitute equation (4) to equation (6), the interactions between molecules can be written as:

$$F_{ij} = \frac{48\varepsilon}{\sigma^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{8}\right]\cdot r_{ij} \tag{7}$$

The model of nanofluid in the present work is composed of water molecules and copper nanoparticle. The L-J potential parameters that are suitable for Cu-H_2O nanofluids can be calculated According to Lorentz-Berthelot mixing rule, which is written as [19]:

$$\sigma_{sl} = \frac{\sigma_{ss} + \sigma_{ll}}{2} \tag{8}$$

$$\varepsilon_{sl} = \sqrt{\varepsilon_{ss}\cdot\varepsilon_{ll}} \tag{9}$$

The L-J potential parameters used in the present work are listed in Table 1.

Table 1. L-J potential parameters for water and Cu-H_2O nanofluids.

Atom 1	Atom 2	ε (g Å/fs^2)	σ (Å)
O	O	1.0568e-028	3.1506
O	H	0	0
H	H	0	0
H	Cu	0	0
O	Cu	8.3251e-028	2.7443
Cu	Cu	6.5582e-027	2.338

2.2 Simulation model

Currently, most work on simulation of nanofluids by MD method employed monatomic Argon as the base fluid. However, the temperature range of liquid Argon is relatively narrow. As a result, the MD simulation results are hard to be compared to experimental results. Based on the above analysis, in the present work water molecules are employed as base fluid.

Due to the complexity of polymers formed by hydrogen bonds between water molecules, currently most potential functions for describing the interactions between water molecules are semiempirical. Frequently-used water potential models include SPCE, SPC, TIP3P, etc. These models basiclly add electrostatic interaction using Coulomb's law and the dispersion and repulsion forces using the L-J potential. Among them, three-site models have three interaction sites, corresponding to the three atoms of the water molecule. Each atom gets assigned a point charge, and the oxygen atom also gets the L-J parameters [20]. The 3-site models are very popular for MD simulations because of their simplicity and computational efficiency. In the present work, SPCE model which is a classical 3-site model is chosen to describe the interactions between water molecules.

The simulation model for single-phase water is consisting of 864 water molecules, which is shown in Fig. 1. And the initial configuration of water molecules follows Face Centered Cubic (FCC) lattice with lattice constant of 29.5666 Å. The model is relaxed for 300000 time steps with time step length of 2 fs. And then the simulation continues to calculate the water thermal conductivity. The nanofluid model contains molecules of 887 with a 1nm copper nanoparticle in the centre. And the volume concentration of nanofluid model is 2.0%. This model is also relaxed for the same relaxation time of 300000 time steps. Monitoring on the internal energy of simulation system indicates the system is balanced after the relaxation, as shown in Fig. 2. The nanofluid model after relaxation is shown in Fig. 3.

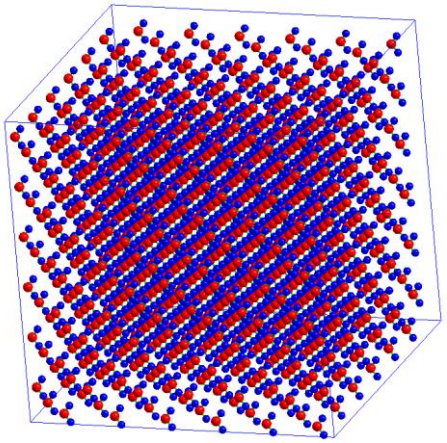

Fig. 1. Simulation model for single phase water.

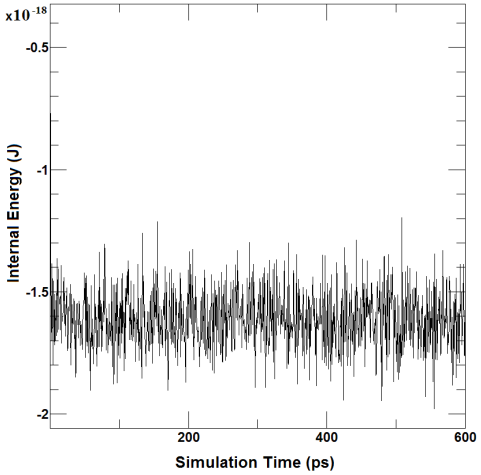

Fig. 2. Internal energy evolution of simulation system.

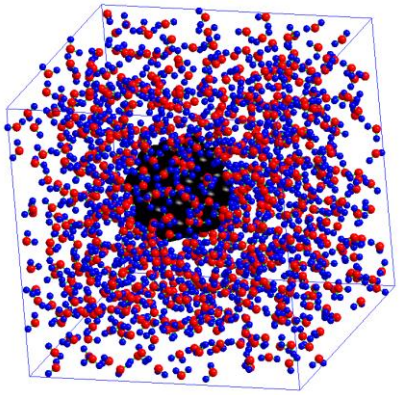

Fig. 3. Simulation model for nanofluid.

3. Results and discussion

3.1 Simulation results of thermal conductivity

In the present work, the models of single phase water and nanofluid are both simulated for 500000 time steps

with time step length of 2*fs*. And the statistical calculation starts from 300000 time steps to the end of calculation. The models are simulated at different temperatures: 293K, 303K, 313K, 323K, 333K, 343K, and thermal conductivities are statistical computed according to Green-Kubo theory [19]. The simulation results for single phase water are shown in Fig. 4. In the figure it could be found that the simulated results for single phase water basically agree with experimental data. At 313K the simulated value is 0.63518 W/m·K, which exactly coincides with the experimental data. The maximum error is 11.4% at 343K. Fig. 5 shows the simulated results for nanofluids, it is found that nanofluid possess higher thermal conductivity compared to that of single phase water at the same temperature. At 313K, the simulated thermal conductivity is 0.85286 W/m·K, which is 34.3% higher compared to single phase water. Whether single phase water or nanofluid, the thermal conductivity is a monotonic increasing function of thermodynamic temperature.

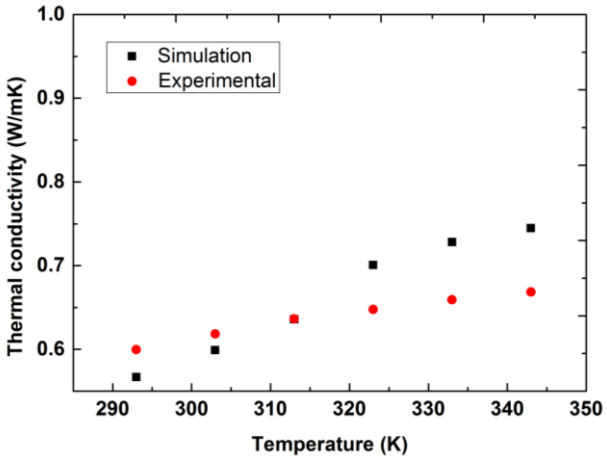

Fig. 4. Comparison of simulated and experimental thermal conductivities for single phase water.

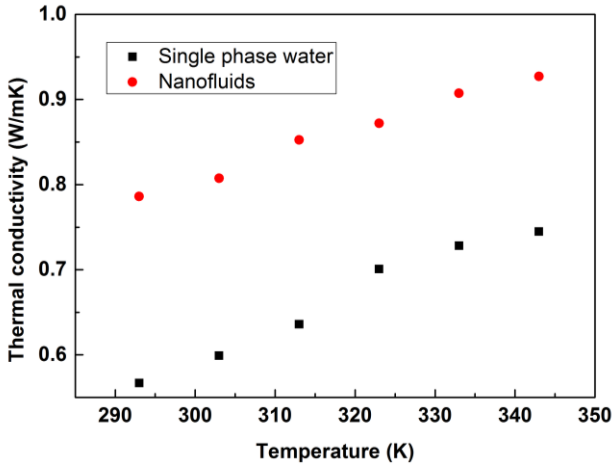

Fig. 5. Comparison of simulated thermal conductivities for single phase water and nanofluids.

3.2 Microcosmic mechanisms for nanofluid thermal conductivity enhancement

3.2.1 Absorption layer

When the naoparticles are dispersed into base fluid, some liquid molecules are absorbed to the solid surface of nanoparticles and form stratified structure which is called absorption layer [18]. It is generally known that the thermal conductivity of solid materials is higher than that of liquid, which is mainly caused by their more ordered distribution. The liquid molecules in the absorption layer have a more even distribution, and therefore the heat conducting in this layer is faster. Thus, this absorption layer plays the role of a fast track between solid nanoparticle and base fluid as the interface resistance is weakened. Therefore the absorption layer is one of the most important mechanisms for explaining the increasing nanofluid thermal conductivity.

Fig. 6 schematically shows the cross-section drawn of nanofluid at a certain simulation time step. In the figure it could be found that there exists one layer of liquid molecules on the solid surface of nanoparticle. Furthermore in this layer the configuration of molecules is obviously more homogeneous. This phenomenon is due to the larger attraction from the solid atoms. Since solid atoms are uniformly distributed, the distribution of liquid molecules that are absorbed by the solid atoms is more ordered. Through tracing the simulation, it was found that once the water molecule is absorbed to the nanoparticle, it will move associated with the nanoparticle and never be far away.

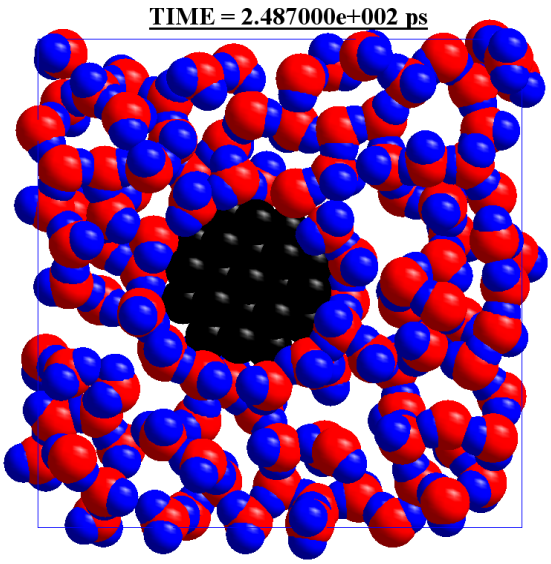

Fig. 6. Schematic diagram of absorption layer.

Fig. 7 shows the statistical calculation results for the number density of absorption layer at different

temperatures. It could be found in the figure that the thickness of absorption layer is about 5 Å. Thermodynamic temperature plays a role in the density of absorption layer. In the figure the curve peak monotonous increases with the increasing temperature, and the curve peak of 353K is the highest. This phenomenon indicates that at higher temperature the liquid molecules are absorbed more densely. High temperature makes molecular motion be more intensely, which improves their change of approaching nanoparticles. And therefore higher temperature is beneficial to molecule absorption.

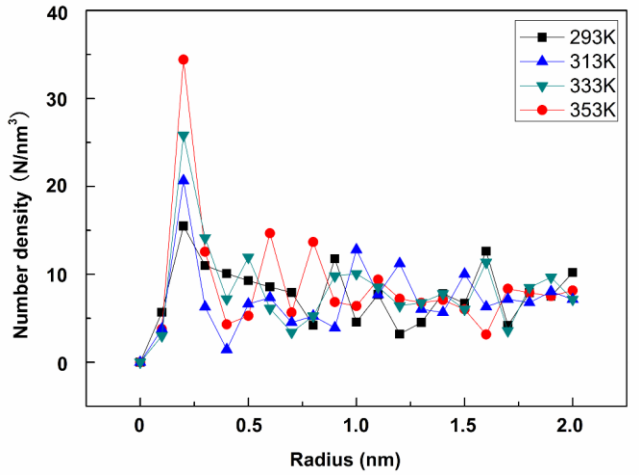

Fig. 7. Influence of temperature for absorption layer around nanoparticle.

3.2.2 Preliminary analysis on the chaotic motion of nanoparticles

When dispersing nanoparticles into the base fluid, these nanoparticles will move chaotically due to their small size and the striking of surrounding molecules. Since the size of a nanoparticle is close to a molecule, the instantaneous speed of nanoparticle' chaotic motion is extremely large. The additional heat transferring caused by the perturbation of nanoparticle motion cannot be disregarded.

Fig. 8 shows the comparison of nanoparticle position at different simulation time steps. In the figure, five copper atoms at the nanoparticle surface are colored by dark color in order to show the nanoparticle motion. Through this figure the chaotic motion of nanoparticle could be qualitatively analyzed. Furthermore, by tracking the simulation it could be found that the nanoparticle is moving ceaselessly. The nanoparticle rotates and moves in the base fluid along with the time evolution. In the simulation, none of the copper atoms broke away from the nanoparticle.

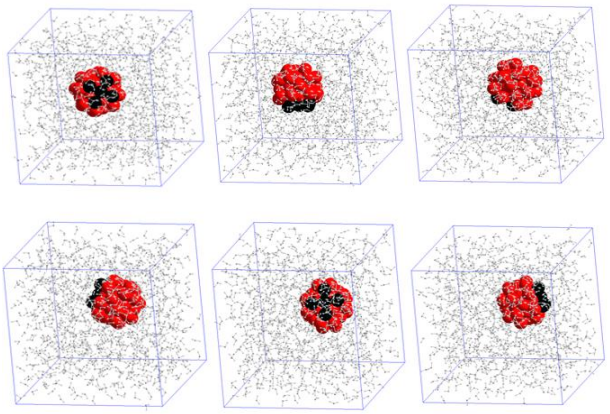

Fig. 8. Chaotic motion of nanoparticles.

4. Conclusions

(1) The present study utilized MD simulations to calculate water-based nanofluid thermal conductivity at different temperatures. And it was found that the nanofluid thermal conductivity increases with the increasing thermodynamics temperature.

(2) The microcosmic mechanisms for the increasing thermal conductivity of nanofluids are investigated. Through tracking the nanoparticle during the simulation, it was found that liquid molecules form a dense absorption layer at the solid surface of nanoparticle. With increased thermodynamics temperature, the absorption layer is denser. The thermal conductivity of absorption layer is higher than that of single phase liquid, and therefore the absorption layer plays the role of a fast track between solid nanoparticle and base fluid as the interface resistance is weakened.

(3) In the simulation it is also found that the instantaneous speed of nanoparticle' chaotic motion is extremely large. As a consequence, the additional heat transferring caused by the perturbation of nanoparticle motion cannot be disregarded.

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