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Nanofluid's Thermal Conductivity Enhancement Investigation by Equilibrium Molecular Dynamics Simulation

Nan Wang [1], Lin Shi [1+], Jun Chen [2] and Haifeng Jiang [1]

[1] Key Laboratory of Thermal Science and Power Engineering of Ministry of Education
Tsinghua University, Beijing, China, 100084

[2] State Nuclear Power Software Development Center, Beijing, China, 100029

Abstract. Nanofluids have been proposed as a route for surpassing the performance of currently available heat transfer liquids in the near future. In this study an equilibrium molecular dynamics simulation was used to investigate the thermal conductivity enhancement of nanofluid. The thermal conductivities of the base fluid and nanofluid were computed via Green-Kubo method. In order to investigate the mechanism of heat transfer enhancement, a new conception TPeV was proposed to describe the transport properties enhancement contribution by unit volume fraction of nanoparticles. The contributions from liquid and solid to the effective thermal conductivity of nanofluid were also computed, and the results showed that the solid's contribution was negligible and the liquid's contribution was dominant. The thermal conductivity of liquid in nanofluid was found to be higher than that of liquid in base fluid. By tracking the positions of the solid and liquid atoms, it was found that a thin layer of liquid was formed at the solid-liquid interface and this layer showed the more ordered structure like solid. The obtaining results indicated that the properties of liquid changed by the nanoparticles may be the mechanism of thermal conductivity enhancement in nanofluid.

Keywords: nanofluid, thermal conductivity, molecular dynamics, Green-Kubo, TPeV, liquid layer.

1. Introduction

Engineered suspensions of nanoparticles in liquids, known recently as nanofluid, have generated considerable interest for their potentials to enhance the heat transfer rate in engineering systems [1,2], while reducing, or possibly eliminating, the issues of erosion, sedimentation and clogging that plagued earlier solid-liquid mixtures with larger particles. It is estimated that more than 300 research groups and companies were engaged in research of nanofluids. In spite of the attention received by this field, uncertainties concerning the fundamental effects of nanoparticles on thermal physical properties of solvent media remain. The thermal conductivity has catalyzed the attention of the nanofluids research community most. As dispersions of solid particles in a continuous liquid matrix, nanofluids are expected to have a thermal conductivity that obeys the effective medium theory developed by Maxwell over 100 years age [3]. However, several deviations from the predictions of Maxwell's have been reported, including a strong thermal conductivity enhancement (TCE) beyond that predicted by Maxwell equation with a nonlinear dependence on nanoparticle loadings [4-6] and a dependence on particle size and shape and fluid temperature [7-10]. Several mechanisms were recently formulated, such as nanoparticle's Brownian motion [11,12], agglomeration of nanoparticles [13-15] and the highly ordered liquid layer around the nanoparticle [13,14,16], to explain these unexpected and intriguing findings.

The macroscopic transport properties of the mixture are dependent on the microscopic exchange of heat and momentum between particles and fluid. When the particle radius is much smaller than the macroscopic transport characteristic scale, even comparable with molecular scale, it is necessary to study each heat-

[+] Corresponding author. Tel.: +86-10-62787613; fax: +86-10-62787613.
E-mail address: rnxsl@mail.tsinghua.edu.cn.

carrier's behaviour to explain the heat transfer mechanism on the micro-level by molecular simulation or quantum mechanics and so on. With the development of computer science, it has been able to simulate directly the behaviours of nanoscale particles, and the computer simulation has become an important tool to investigate the mechanism in many processes. Molecular dynamics (MD) simulation is a determinate method based on the rule of molecular motions, which requires and provides complete informations about molecular position and momentum at each time. MD is extremely useful for investigating liquids and solids (especially liquids) from a microscopic point of view and for calculating thermophysical properties of fluids.

In this paper, a Cu/Ar nanofluid system was established by using MD simulation. The thermal conductivities of the base fluid and nanofluids with different volume fractions of nanoparticles were calculated by using equilibrium molecular dynamics (EMD) simulation. In order to investigate the mechanism of TCE, a new conception TPeV was proposed to describe the transport properties (thermal conductivity here) enhancement contribution by unit volume fraction of nanoparticles. The contributions from liquid and solid to the effective thermal conductivity of nanofluid respectively were also computed. The density distribution of the liquid from the center of the nanoparticle and the thickness of ordered liquid layer were also investigated.

2. Molecular Dynamics Model

2.1. Simulation Details

In this work, a base fluid model of Ar and a nanofluid model of Cu particles in Ar fluid were developed. In our simulation, the interatomic interactions between solid Cu and liquid Ar were all modeled by pairwise Lennard-Jones (LJ) potential with appropriate Lennard-Jones parameters,

$$\varphi(r_{ij}) = 4\varepsilon\left[\left(\sigma/r_{ij}\right)^{12} - \left(\sigma/r_{ij}\right)^{6}\right] \tag{1}$$

where ε and σ are energy and length parameters, respectively, φ is the interatomic potencial, and r_{ij} is the interatomic distance between atoms i and j. For Ar, the LJ parameters ε and σ are equal to 1.654×10^{-21}J and 0.3405nm, respectively, and for Cu, the LJ parameters ε and σ are equal to 65.625×10^{-21}J and 0.23377nm [17], respectively. The parameters σ_{sl} and ε_{sl} for the solid-liquid interactions are calculated by Berthlot mixing rule [18]:

$$\sigma_{ls} = \left(\sigma_{ll} + \sigma_{ss}\right)/2, \quad \varepsilon_{ls} = \sqrt{\varepsilon_{ll}\varepsilon_{ss}} \tag{2}$$

where the subscripts s and l refer to solid and liquid. In this study all the parameters for liquids were set equal to unity and taken as reference and simulations were performed in nondimensional units. NVT ensemble was used in the simulations, which meant the total number of atoms, the system volume, and the fluid temperature were constant throughout the simulation. To improve computational efficiency, we chose the cutoff radius equal to $4.5\sigma_{ll}$, which meant the two atoms had a negligible interaction when their distance was further than $4.5\sigma_{ll}$. Velocity Verlet algorithm was used as the integration scheme.

The thermal conductivity of Ar fluid was calculated by using EMD simulation via Green-Kubo (GK) theory. The GK formula for thermal conductivity can be written as [18]

$$\lambda = \frac{1}{3k_B V T^2}\int_0^\infty \left\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\right\rangle dt \tag{3}$$

where λ is the thermal conductivity, V the system volume, T the temperature, k_B the Boltzmann constant, $\boldsymbol{J}$ the heat flux vector, and the angular brackets denote the ensemble average over the time, and $\left\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\right\rangle$ is the heat flux autocorrelation function (HACF). The heat flux vector was calculated as [18]

$$\mathbf{J}(t) = \sum_i \frac{1}{2} m_i v_i^2 \mathbf{v}_i + \sum_i \sum_{j>i} \varphi(r_{ij})\mathbf{v}_i + \frac{1}{2}\sum_i \sum_{j\neq i} \mathbf{r}_{ij}\left(\mathbf{f}_{ij}\cdot\mathbf{v}_i\right) - \sum_i \mathbf{v}_i h \tag{4}$$

where m is the atomic weight, v the atomic velocity, $\boldsymbol{r}_{ij}$ the distance vector from atoms i to atom j, $\boldsymbol{f}_{ij}$ the force on atom i due to atom j, h the enthalpy per particle. For the two component system in our simulation we use (5), an extended form of (4), to calculate the heat flux vector $\boldsymbol{J}$ according to

$$\mathbf{J}(t)=\sum_{\alpha=1}^{2}\sum_{i}^{N\alpha}\left(\frac{1}{2}m_{\alpha}v_{j\alpha}{}^{2}\right)\mathbf{v}_{i\alpha}-\frac{1}{2}\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\sum_{i=1}^{N\alpha}\sum_{j\neq i}^{N\beta}\left[\mathbf{r}_{i\alpha j\beta}\frac{\partial\varphi\left(r_{i\alpha j\beta}\right)}{\partial r_{i\alpha j\beta}}-\varphi\left(r_{i\alpha j\beta}\right)\mathbf{I}\right]\mathbf{v}_{i\alpha}-\sum_{\alpha=1}^{2}h_{\alpha}\left(\sum_{i}^{N\alpha}\mathbf{v}_{i\alpha}\right) \quad (5)$$

The subscripts α and β denote two kinds of particles (solid and liquid). N_{α} and N_{β} are the number of particles of kinds α and β.

In our model, the thermal conductivity of Ar fluid was simulated varying temperature from 85K to 130K, and then one nanoparticle or two was considered in Ar fluid. To start with, all the atoms in the nanofluid system were arranged in a regular face center cubic lattice. Periodic boundary condition was applied in all directions of three-dimensional cubic simulation cell. A total of 1372 atoms were considered in the system. The nanoparticle loadings are from 0.07% to 4.66%. The simulation was continued for 500 000 time steps. Each time step was 4fs. Initial 100 000 time steps were ignored and to allow the system to reach equilibrium. After 100 000 time steps, the heat flux vector was calculated at each time step according to (5). Then the thermal conductivity was calculated according to (3). In this paper, a total number of 400, 000 integration time steps were used to product HACF extended up to 10ps with a resolution of 16fs.

2.2. Validation of model

It is necessary to validate the model with some acknowledged results. Sarkar [17] observed that after 1372 atoms, the thermal conductivity of nanofluid converged well as compared to 500 atoms for Ar fluid. Hence we calculated the thermal conductivity of liquid Ar varying the temperature from 85K to 130K, and density from 1407.1kg/m^3 to 1039.5kg/m^3 with 1372 Ar atoms. Table 1 gives the thermal conductivity of the simulation results and reference data [19] in different temperature and density. From Table 1, it is found that the simulation results are in good agreement with reference data. All of the relative errors are less than 3%. So it is feasible to use this model to simulate the thermal conductivity of nanofluid.

Table 1: The thermal conductivity of the simulation results with reference data in different conditions

State points	T (K)	Density (kg/m^3)	λ_{MD} (mW/m.K)	λ_{Ref} (mW/m.K)[19]	Relative error (%)
1	85	1407.1	130.85	128.69	1.6
2	90	1375.7	124.88	122.07	2.3
3	100	1310.96	111.33	108.87	2.2
4	110	1240.08	97.70	95.888	1.9
5	120	1160.36	84.80	83.208	1.9
6	130	1039.5	69.91	70.891	1.4

2.3. Results and Discussions

The thermal conductivities of nanofluids were simulated by the same method with nanoparticle loadings from 0.07% to 4.66% by volume fraction at the temperature of 85K. The results can be seen in Table 2. In order to investigate the mechanism of TCE further, a new conception TPeV was defined as the ratio of TCE range to the volume fraction of nanoparticles in nanofluid. The formula can be written by

$$\mathrm{TPeV}=(C_{eff}/C_{f}-1)\big/Vol \quad (6)$$

where C means transport properties such as thermal conductivity, viscosity, and diffusion coefficient. Vol is the volume fraction of nanoparticles. The subscripts *eff* and *f* denote nanofluids and base fluid, respectively. TPeV means Transport Properties (thermal conductivity here) Enhancement contribution by unit Volume fraction of nanoparticles. TPeV can make quantitative analysis of various factors' effects on the heat transfer properties. TPeV calculated by (6) can also be seen in Table 2.

From Table 2, it is clearly that the TCE range increases with the increasing volume fraction except Status 6, while TPeV has decreasing trend with the increasing volume fraction. It should be pointed out that, Status 1, 2, 4, and 6 has one nanoparticle whose size is increasing, and their TPeV is decreasing. Status 3 has two nanoparticles whose size is the same as Status 2, and their TPeV is close. State 4 and 5 are similar to State 2 and 3. So TPeV also has decreasing trend with the increasing nanoparticle size. That is to say, with the bigger nanoparticle size, the less contribution of thermal conductivity enhancement by unit volume fraction of nanoparticles. In our opinion, the size and the volume fraction of nanoparticles are both very important

factors and TPeV can synthesize the two factors. It is mentioned that, although State 6 has higher volume fraction than State 5, the TCE is a bit lower. This may have two reasons. One is the nanoparticle size of State 5 is smaller. The other is Status 5 has two nanoparticles, which may induce stronger interaction between nanoparticles or between nanoparticles and liquid. The values of TPeV show us that the nanoparticle loadings should have an optimum volume fraction district, in which TPeV should be stable or at least fluctuate slowly. The application of TPeV can help us to find the optimum volume fraction district.

Table 2: The effective thermal conductivity of nanofluid with different volume fractions in 85K

State points	V% of NP	λ_{MDnf} (mW/m.K)	$\lambda_{eff}/\lambda_{f}$-1 (%)	TPeV
1	0.07	131.55	2.23	30.48
2	0.58	140.31	9.03	15.48
3	1.17	148.79	15.62	13.41
4	1.97	164.82	28.08	14.28
5	3.93	190.55	48.07	12.22
6	4.66	178.10	38.40	8.24

The contributions from liquid and solid to nanofluid's thermal conductivity of were also computed. Fig. 1 shows the contribution from liquid (TC-lc) and solid (TC-sc) compared to the thermal conductivity of nanofluid (TC) with the time at State 5. From Fig. 1, it is easy to find that the solid's contribution is very small although the solid-solid interaction is the strongest in the system. The liquid's contribution plays a dominant role in the effective thermal conductivity.

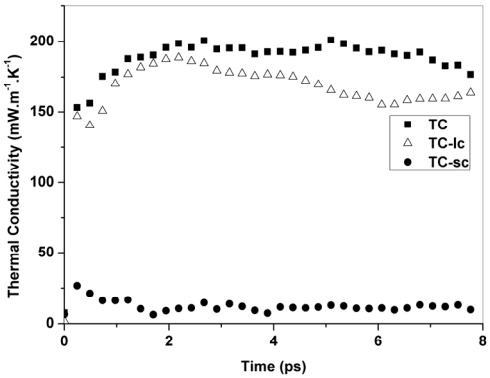

Fig. 1: The contribution from liquid and solid to nanofluid's thermal conductivity at State 5

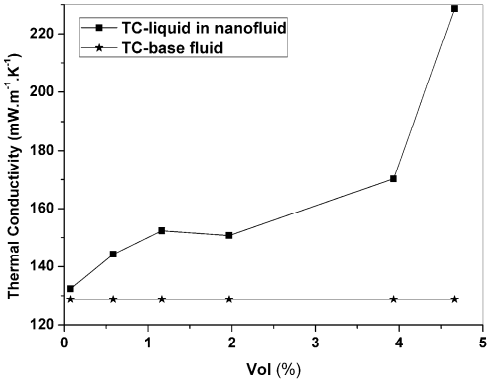

Fig. 2: The thermal conductivity of liquid in nanofluid with different nanoparticle loadings

The thermal conductivities of liquid in nanofluid were also calculated via GK theory with different nanoparticle loadings (shown in Fig. 2). From Fig. 2, it is obviously that the thermal conductivity of liquid in nanofluid is higher than that of base fluid and it has increasing trend with the increasing volume fraction. The reason for this is the property of liquid in nanofluid has been changed by the nanoparticles. The modification in liquid improves with increasing nanoparticle loadings. It is well known that the thermal conductivity of solid Cu is much greater than the base fluid Ar, but the solid's contribution to nanofluid's thermal conductivity is negligible. In conclusion, the nanoparticle itself plays a tiny role to the nanofluid's thermal

conductivity, and the important mechanism is the nanoparticles have changed the base fluid's properties.

In order to know the influence of nanoparticles on changing the base liquid's properties, the positions of the solid and liquid atoms were tracked with time. According to observing the traces of the selected atoms, it can be seen that most liquid atoms at the solid-liquid interface always move with the nanoparticle. However, a bit of liquid atoms move away from the nanoparticle. Because the interaction between Cu and Ar atoms is stronger than that between Ar atoms, some Ar atoms are attracted to and stick to the nanoparticle. To prove the existence of a liquid layer at the solid-liquid interface, the density distribution of Ar atoms from the center of the nanoparticle was investigated. The number density of the fluid is defined as,

$$n = \Delta N / \Delta V \tag{7}$$

The simulation space was divided into many spherical shells from the center of the nanoparticle, and ΔN is the number of Ar atoms within the shell's volume ΔV. Fig. 3 gives out the density distribution of Ar atoms at the average of different time after the equilibrium state is reached. The independent variable r is the distance from the mass center of nanoparticle. The dependent variable n / n_0 is the relative number density of Ar atoms over the number density of pure Ar n_0. The nanoparticle's radius is 1.0nm and the temperature is 85K. From Fig. 3, it is found that the density of Ar atoms is not uniform in the simulation space. A liquid layer at the solid-liquid interface was observed. The thickness of the layer is about 1.0nm (including the first three peaks), which is closely consistent with the reference data [20-22]. Keblinski [14] offered the liquid layering around the particles is one of the mechanisms for the anomalous enhancement behaviour seen in nanofluid. The liquid molecules form a layer around the solid particles and thereby enhancing the local ordering. Since phonon transfer in crystalline solid is very effective, such local ordering in the liquid can lead to enhanced transport. The ordering of liquid can also change the liquid's properties, and improve the thermal conductivity of liquid, which enhances the nanofluid's heat transfer property.

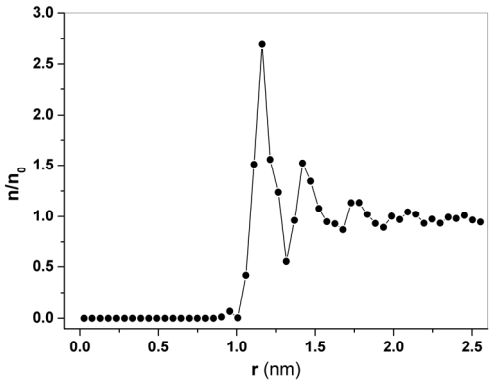

Fig. 3: The density distribution of Ar atoms at the average of different time

3. Conclusions

According to the good agreements between the simulation results and reference data, it is found that our simulation method is effective and credible to calculate the thermophysical properties of nanofluid. The simulation results showed that the TCE of nanofluid increased generally with increasing nanoparticle loadings and the TPeV showed decreased trend with increasing nanoparticle size and increasing volume fraction. The application of TPeV showed us the nanoparticle loadings should have an optimum volume fraction district and helped us to find the district. The solid's contribution to the effective thermal conductivity of nanofluid was found to be neglected and the liquid's contribution played a dominant role in TCE. The thermal conductivity of liquid in nanofluid was simulated to be higher than that of the base fluid, and it showed increasing trend with the increasing volume fraction. It is because the properties of liquid have been changed due to the presence of nanoparticle. Through the density distribution of Ar atoms from the center of the nanoparticle, a liquid layer was found to form at the solid-liquid interface. The thickness of the liquid layer is about 1.0nm. The liquid layer also validated that the liquid structure became more ordered in the presence of nanoparticle. So it is not the solid's own properties but the liquid's changed properties due to the nanoparticles which improve the heat transfer in nanofluid and cause higher thermal conductivity of nanofluid. This is the main mechanism for enhanced thermal transport in nanofluids in our simulations.

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