Study on the Microscopic Mechanism of Adsorption Layer on the Surface of Particles in Nanofluids

Liang Zhang¹, Linchao Tian¹, Anlong Zhang¹

¹College of Vehicles and Energy, Yanshan University, Qinhuangdao, 066004, China

e-mail: zhangliang402@ysu.edu.cn

Abstract. In this paper, the method of molecular dynamics simulation is used to study the Cu-Ar nanofluid. It is found that when Cu nanoparticles of different volume fractions are added to liquid Ar, the thermal conductivity of the nanofluid can increase by 32.1%; adding different sizes of Cu nanoparticles. In the case of particles, the thermal conductivity of nanofluids can increase by 15.2%. On this basis, the strengthening mechanism of the thermal conductivity of the nanofluid was analyzed from a microscopic point of view, and it was found that the microstructure of the base fluid has changed after adding nanoparticles. The degree of change of the microstructure of the base fluid is greatly affected by the size of the nanoparticles. The closer to the nanoparticle base fluid, the more significant the microstructure changes. The thickness of the adsorption layer was calculated by dividing the surface of the nanoparticle and tracking the movement trajectory of Ar atoms in these areas and counting changes in the number of argon atoms. It was found that the adsorption layer was a key factor leading to the improvement of the thermal conductivity of nanofluids.

1. Introduction

Choi and Eastman [1] first began to study nanofluids in 1995. In recent years, many scholars have conducted research on the microscopic mechanism of nanofluids to improve thermal conductivity [2]. Javanmardi and Jafarpurt [3] used the EMD method to analyze the effect of the thermal conductivity of the carbon nanotube-water nanofluid, and found that both the concentration and temperature affect the nonlinear change of the effective thermal conductivity of the fluid. Lee et al. measured the thermal conductivity of nanofluids containing Al2O3 and CuO nanoparticles in water and ethylene glycol [4]. They used a volume fraction of 1~5% and achieved a thermal conductivity improvement of up to 20%. Leong [5] et al. assumed that the thickness of the adsorption layer was 1 nm, and believed that the adsorption layer on the surface of the nanoparticles and the size of the nanoparticles were the main reasons for the increase in the thermal conductivity of nanofluids.

In summary, there are still controversies about the effect of the adsorption layer on the surface of nanoparticles and the size of the nanoparticles on the thermal conductivity of nanofluids (NF), and there is a lack of research on the thickness of the adsorption layer on the surface of nanoparticles (NP) in previous studies. Taking Cu-Ar nanofluid as an example, this paper first introduces the basic principles and model establishment of MD simulation, analyses the factors that affect the thermal conductivity of nanoparticles, and further studies the trajectory of argon atoms on the surface area of nanoparticles. Through the analysis of Cu nanoparticles, the change in the number of argon atoms on the surface and the microstructure near the surface of the particles are used to estimate the thickness of the adsorption
layer. The results of this study can provide a reference for the application of nanofluids in the cooling oil cavity.

2. Theory and model

2.1. Potential parameter of atoms
Molecular Dynamics Simulation (MDS) method is a common method for studying the heat conduction of nanofluids. This study used a set of open source molecular dynamics simulation package lammps (Large-scale Atomic/Molecular Massively Parallel Simulator) developed by Sandia National Laboratory in the United States. The selection of the potential function between atoms uses Lennard-Jones (LJ) [6,7] the expression is:

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

In the formula, \( r \) is the distance between pairs of atoms; \( \varepsilon \) and \( \sigma \) are potential energy parameters, \( \sigma \) represents the distance between atoms, and the value of \( \varepsilon \) can reflect the depth of the potential energy curve, \( r_{ij} = r_j - r_i \), and \( r_i \) is the position vector of the \( i \)-th atom. For the potential between Cu-Cu, the LJ parameter is the current potential function that consumes fewer computing resources.

For the copper-argon NF, the selection of LJ parameters \( \varepsilon \) and \( \sigma \) are shown in Table 1 [8]

| Atom pair | \( \sigma/\text{nm} \) | \( \varepsilon \times 10^{-28} \text{J} \) |
|-----------|------------------|------------------|
| Ar-Ar     | 0.3405           | 1.654            |
| Cu-Cu     | 0.2338           | 65.581           |
| Cu-Ar     | 0.2871           | 10.415           |

The potential parameter between Cu-Ar can be calculated by Lorentz-Berthelot mixing rule [9]:

$$\sigma_{\text{Cu-Ar}} = \frac{\sigma_{\text{Cu}} + \sigma_{\text{Ar}}}{2}$$

$$\varepsilon_{\text{Cu-Ar}} = \sqrt{\varepsilon_{\text{Cu}} \varepsilon_{\text{Ar}}}$$

2.2. Thermal conductivity of nanofluid
The typical method for calculating the thermal conductivity of NF is equilibrium molecular dynamics (EMD). The Green-Kubo method links the fluid thermal conductivity with the heat flow autocorrelation function, so the thermal conductivity is calculated by the time integral of the heat flow autocorrelation function [10]:

$$\kappa = \frac{1}{3V k_B T^2} \int_0^{\infty} \langle J_q(\tau) J_q(0) \rangle d\tau$$

Where \( k_B, V \), and \( T \) are Boltzmann's constant, volume and temperature, respectively, \( \langle J_q(\tau) J_q(0) \rangle \) is the heat flow autocorrelation function, \( \langle \rangle \) represents the time average, \( J_q(\tau) \) represents the time \( \tau \) instantaneous heat flow vector.

3. Test Results and Discussions
The initial model of the system is a cubic simulation box, which is filled with liquid argon atoms in the fcc lattice arrangement of liquid argon. Place a certain volume fraction of copper NP in the simulation box, that is, select the position of the copper NP that needs to be placed in the liquid argon system, then delete the same volume of liquid argon atoms, and insert the copper NP to obtain the copper-argon NF molecule Kinetic model, as shown in Fig. 1, the NP volume fraction is 1%, and the blue copper NP is surrounded by liquid argon atoms.
3.1. Algorithm verification

The thermal conductivity of the pure liquid argon system calculated in this paper is 0.128 W/(m•k), which is in good agreement with the calculation result of 0.127 W/(m•k) in the literature [11]. It shows that the accuracy of the simulation method is better and feasible. The thermal conductivity of NF with 1% NP is further simulated, and the result is 0.138 W/(m•k). As shown in Fig. 2, the heat flow autocorrelation function curve of NP can also be found in the figure. There is a certain periodic oscillation before 300 ps, which shows that after adding NP, the instantaneous heat flow in NF has changed.

![Fig. 2 Thermal conductivity and heat flow autocorrelation function curve of 1% volume fraction NF and pure liquid argon system](image)

3.2. Influence of Nanoparticle Volume Fraction and Size on Thermal Conductivity of Nanofluid

In the simulation system, Cu NP with a volume fraction of 1% ~ 6% was added successively, and the corresponding NPs contained Cu atoms of 87,174,261,348 and 435,522, and the simulation time was 4000 ps.

The influence of different NP volume fractions on the thermal conductivity of nanofluids is shown in Table 2. It can be seen from the table that, compared with the thermal conductivity of liquid argon system, the NF of 1%~4% volume fraction has a particularly significant impact on the thermal conductivity. Significantly, with the increase of the volume fraction, the thermal conductivity increased from 1.078 W/(m•k) to W/(m•k) times. The influence of 4%~6% volume fraction of NP on the thermal conductivity began to weaken compared with 1%~4%, and the increase rate decreased sharply.

| φ (%) | κ (W/(m•k)) | rate of change |
|-------|-------------|---------------|
| Pure ar | 0.1281 | 1 |
| Cu-1.0% | 0.1381 | 1.078 |
| Cu-2.0% | 0.1525 | 1.191 |
| Cu-3.0% | 0.1642 | 1.282 |
| Cu-4.0% | 0.1681 | 1.312 |
| Cu-5.0% | 0.1687 | 1.317 |
| Cu-6.0% | 0.1692 | 1.321 |
The radius of NP in the system is 1.03nm, 1.26nm, 1.50nm, and the volume fraction is 1%. At a temperature of 86K, the effect of different sizes of NP on the thermal conductivity of NF at 1% volume fraction is shown in Fig.3(a). It can be seen from the figure that the thermal conductivity of NF is higher than that of the base fluid, and it is also found that as the radius of NP increases, the thermal conductivity of NF gradually decreases. The effect of NP size on the increase of thermal conductivity is shown in Fig. 3(b). It is found that with the increase of NP size, the increase of NP thermal conductivity gradually decreases. That is, the smaller the NP radius, the better the thermal conductivity of nanofluid.

Fig.3 (a) The effect of nanoparticle size on the thermal conductivity of nanofluids, (b) the effect of nanoparticle size on the increase in thermal conductivity

3.3. Adsorption layer on particle surface
An important mechanism for the thermal conductivity of NF to be stronger than that of conventional fluids is that there are a number of base liquid atoms on the surface of NP that are similar to the particle atomic arrangement. In this study, we tracked the sphere with NP as the centre and the NP radius as the sphere radius and gradually increasing the radius. As shown in Fig. 4. It can be found from the figure that the Ar atoms within 0.4nm from the NP surface have been following the movement of the NP, but at a distance of 0.5nm from the NP surface a small part of Ar atoms begin to escape. Although the Ar atom escape phenomenon begins at 0.5nm from the NP surface, this does not mean that the thickness of the NP adsorption layer is 0.5nm, because these atoms are just the arrangement of argon atoms at the initial moment. From Fig. 5 (Fig. 5a represents the trajectory of a Cu atom on the NP surface, Fig. 5b represents the trajectory of an Ar atom closer to the Cu atom), it can be seen that the trajectories of Cu atoms and Ar atoms are basically synchronized, which is due to the distance. The closer the NP is, the greater the force of the NP is applied to the Ar, and the trajectory in Fig. 5c is the Ar atom farther away from the Cu atom. Although the atom is not bound by the Cu atom, the density of the trajectory is quite different. It will move to the surface of the NP and move synchronously with the NP for a period of time. This means that although a small part of Ar atoms begin to escape at a certain distance from the surface of the NP, more atoms will be added to make the thickness of the adsorption layer increase instead.

Fig. 4 Argon atom adsorption layer in 0.4nm and 0.5nm thin layers on the surface of nanoparticles at 0ps, 50ps, 100ps and 120ps
In order to further analyze the atomic number density distribution in NF, in the whole research process, starting from the center of the spherical NP, the atomic number density in each spherical shell with a thickness of 0.1nm is counted and analyzed. It is found that the base liquid atoms adsorbed by NP will follow NP moves together, the closer the NP is, the greater the atomic number density, as shown in Fig. 6 (the atomic number density distribution at different moments in NF with a NP radius of 0.7nm and a volume fraction of 1.5%). It can also be seen from the figure that obvious valleys appear at 0.15nm and 0.35nm respectively, and obvious peaks appear at 0.25nm and 0.45nm respectively, and there are still peaks and valleys alternately appearing after 0.45nm on the NP surface until When the distance from the particle surface is greater than 12.5nm, the atomic number density tends to be constant, which indicates that there is a thin layer of Ar atoms between the NP surface and the Ar atoms that are not affected by NP, and this fluctuation is leaving the surface of the nanoparticle. It still exists after knowing that about 1.2nm will become constant, which shows that the thickness of this thin layer is about 0.5nm.

4. Conclusion

In this paper, molecular dynamics methods are used to analyze the microscopic mechanism of Cu-Ar nanofluid thermal conductivity improvement. Based on the above analysis, the conclusions are as follows:

(1). When the volume fraction is large, the thermal conductivity of the nanofluid can increase by 32.1%, and the thermal conductivity of the nanofluid increases with the volume fraction of the nanoparticle; when the size of the nanoparticle is small, the thermal conductivity of the nanofluid can increase by 15.2 %, and the thermal conductivity of nanofluids decreases with the increase of nanoparticle size.

(2). There is a thin layer of Ar atoms on the surface of Cu nanoparticles. By analyzing the changes in the number density of Ar atoms in the surface area of Cu nanoparticles, it is inferred that the thickness of this thin layer of Ar atoms is about 0.5nm, and the thickness of the Ar atoms on the surface of the particles is 0.4nm. Ar atoms will always follow the movement of the particles. After 0.4nm, the Ar atoms on the surface of the particles begin to escape. And this thin layer is a key factor in improving the thermal conductivity of nanofluids.

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