Molecular dynamics simulation of the microscopic interaction in Cu/water nanofluid

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Abstract. With the gradual increase in internal combustion engine load, the heat in the cooling oil cavity has been insufficient to remove too much heat in a timely manner. The excellent thermal conductivity of nanofluids can be used to consider solving such problems. In this paper, the molecular dynamics simulation of the microscopic effect of the particles in the Cu/water nanofluid on the base fluid is carried out by the equilibrium molecular dynamics method. By analyzing the density distribution of various atoms in the nanofluid and the radial distribution function between the base fluid atoms, Cu-H and Cu-O atom pairs, it is found that the main reason for the influence of the nanoparticles on the base fluid is in the area near the Cu particles. The base fluid atoms have an effect, which changes the arrangement of these atoms, and the O atoms around the nanoparticles are closer to the surface of the Cu particles, and the H atoms are slightly away from the surface of the particles.

1. Introduction

In 1995, Choi[1~3] et al. suspended nano-sized solid particles in a conventional fluid to obtain a nanoparticle suspension (nanofluid), and found that this suspension has different thermophysical properties from conventional fluids. In particular, the thermal conductivity of nanofluids is higher than that of conventional fluids. Many scholars at home and abroad have gradually carried out experimental and numerical simulation research on the heat transfer of nanofluids. In the early days, Li Qiang [4] et al. tested the flow and heat transfer performance of copper-water nanofluids through heat conduction experiments, and found that in the range of Reynolds=800~25000, 2% volume fraction of nanoparticles increased the thermal conductivity of the fluid by 60 % Conclusion; afterwards, the thermal conductivity of deionized water-copper, motor oil-aluminum and deionized water-aluminum were experimentally studied using the transient hot wire method, and the results showed that adding nanoparticles to the liquid can increase the thermal conductivity of the fluid and the thermal conductivity increases with the increase of particle volume fraction.

Marco [5] et al. studied the delamination phenomenon of the liquid-solid interface of Cu and CuO/water nanofluids, and the delamination of the base liquid appears on the surface of metal particles. Ali Rajabpour [6] et al. carried out molecular dynamics simulations on the specific heat capacity of Cu-water nanofluids and found that the specific heat capacity of nanofluids decreased with the increase of particle volume fraction. Wang Baohe [7] and others also performed molecular dynamics simulations on the transfer characteristics of Cu-water nanofluids. They found that the thermal conductivity and viscosity of nanofluids are positively correlated with temperature rise, and the thermal conductivity varies with the energy factor of the particles. Increase while the viscosity is basically unchanged.

In summary, the movement and distribution of water molecules on the surface of nanoparticles in...
Cu/water nanofluid have a great impact on the entire system and is the main reason for changing the properties of the base fluid. Therefore, this article will study the microscopic effect of different Cu nanoparticle sizes in the same volume fraction of water-based nanofluid, and analyze the effect of Cu particles on the atoms of the base fluid.

2. Simulation method and system

2.1. Model building
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 [8] (Large-scale Atomic/Molecular Massively Parallel Simulator) developed by Sandia National Laboratory in the United States. The visualization program uses VMD[9] (Visual Molecular Dynamics, VMD); the modeling of Cu/water nanofluid (Nanofluid, NF) uses Packmol[10] tool. Three different nanoparticle (NP) sizes: 0.7nm, 0.9nm, 1.1nm are used for analysis in the same volume fraction 1.5% cube box, the temperature is 298.15K, the parameters in the system are shown in Table 1. As shown, Figure 1 is a schematic diagram of the nanofluid system.

![Fig.1 Nanofluid model: Cu is the blue sphere in the middle surrounded by water molecules](image)

| NP Size/ nm | Box Size/ Å³ | Cu Atom Num. | H₂O Mol. Num. | φ/% |
|-------------|--------------|--------------|---------------|-----|
| 0.7         | 45.754³      | 122          | 2858          | 1.5 |
| 0.9         | 58.826³      | 261          | 5956          | 1.5 |
| 1.1         | 71.899³      | 471          | 11980         | 1.5 |

The simulation system adopts periodic boundary conditions, the step length of the simulation system is 2fs, the long-range electrostatic force adopts the PPPM (Particle-Particle-Particle-Mesh) method, and the bond angle and bond length in the water molecule are fixed by Shake algorithm. In the simulation, it is used to relax the system for 1000 ps under the NPT ensemble, then the temperature is controlled for 10 ps million steps under the NVT ensemble, and finally 2000 ps is calculated under the NVE ensemble.

2.2. Potential parameter of atoms
The selection of the potential function between atoms uses Lennard-Jones(LJ)[11,12], the expression is:

\[ U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \] (1)

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 less computing resources.

The potential parameter between Cu-water and water-water can be calculated by Lorentz-Berthlo mixing rule [13]:

$$\sigma_{Cu- Ar} = \frac{\sigma_{Cu} + \sigma_{Ar}}{2}$$  \hspace{0.5cm} (2)

$$\varepsilon_{Cu- Ar} = \sqrt{\varepsilon_{Cu} \cdot \varepsilon_{Ar}}$$  \hspace{0.5cm} (3)

The parameters of the force between atoms in the system are shown in Table 2:

Table 2 Force field parameters between atoms

| Pair     | $\sigma$/nm | $\varepsilon$/Kcal/mol |
|----------|-------------|------------------------|
| Cu-Cu   | 2.338       | 9.439                  |
| H-H     | 0.000       | 0.000                  |
| O-O     | 3.165       | 0.155                  |

2.3. Radial distribution function

The radial distribution function (rdf) describes the probability of the particle under study appearing in a sphere with a reference particle radius $r$. It is a characteristic physical quantity that represents the microscopic arrangement of fluids and solids. It represents a certain particle $r$ to $\Delta r$ The average number of particles in the interval, the expression is:

$$g_{\alpha\beta}(r) = \frac{V}{N_\alpha N_\beta} \left( \sum_{i=1}^{N_\alpha} n_{\beta}(r, \Delta r) \right) 4\pi r^2 \Delta r$$  \hspace{0.5cm} (4)

Which, $V$ is the volume of the system, $N_\alpha$ and $N_\beta$ indicate the number of two kinds of particles, and $n_{\beta}(r, \Delta r)$ indicates the number of $\beta$ particles in the interval from $\alpha$ particle $r$ to $\Delta r$.

3. Results and analysis

3.1. Model validation

In order to verify the accuracy of the model, the pure water system was simulated under standard conditions ($T=298.15$, $P=1$ atm). 5057 water molecules are in a rectangular box with a system of $44*44*88$, as shown in Figure 2. Shown. In the initial 300,000 steps of 600 ps, the temperature, pressure, total energy, and density of the system converge well. It shows that this research has adopted a more effective calculation method.
3.2. Nanofluid density distribution and radial distribution function (rdf)

In order to analyze the influence of NP on the base fluid, this article calculates the density distribution in NF. By taking the center of the NP as the center of the sphere and gradually increasing the radius with an increasing rate of 1 Å, a number of spherical shells with an interval of 1 Å are obtained, and the number of atoms in each two spherical shells is counted to obtain the atomic number density in this spherical shell. Due to the difference in system size, the radius of the spherical shell that can be increased by different systems is different. As shown in Figure 3, it can be seen that the density distribution of NF in the three systems is not the same. The atomic number density changes the most in NP. The valley value within 0.1nm~0.5nm is due to the distance between atoms is too close. It exhibits repulsive force, causing the number density to decrease; the peak value is due to the gravitational force of the interatomic force with the increase of the distance between atoms, which causes the number density to increase, and the larger the NP size, the more obvious the gravitational force between atoms, which is due to Cu atoms. The larger the number, the greater the force between atoms. This kind of fluctuation will gradually flatten as the radius of the spherical shell gradually increases. This is due to the increasing distance between the atoms and the smaller the force between them. It can also be found that there are fluctuations in the number density from the surface of each particle to the next distance, which shows that the NP has an effect on the base liquid atoms on its surface, and the part of the base liquid atoms that are affected is weaker than the interaction between NP atoms is stronger than that between base fluid atoms. And for 0.7nm NP, the degree of change in the number density of base fluid atoms on the surface is greater than that of 0.9nm and 1.1nm NP surface number densities, which indicates that NPs of different sizes have different effects on the base fluid of the system.

Fig. 3 Density distribution in different nanofluid systems

The difference in density distribution of nanofluids is mainly due to the effect of NP on the base fluid, which changes the microscopic arrangement of atoms in NF. So this paper analyzes the rdf of each atom pair in the base fluid in NF, as shown in Figure 4. Figure 4 (a), (b), (c) respectively represent the rdf between HH and OO atom pairs in NF. It can be seen that there is no big difference in the rdf of the three systems of base liquid atom pairs in NF, only the H,O atom. The first peak of rdf decreases with the increase of NP size, which indicates that the probability of an O atom near an H atom in a small NP system is greater.
Fig. 4 Radial distribution functions between H and O atoms in the three systems

Figure 5 shows the rdf distribution curves of Cu-H and Cu-O atom pairs in the three NF systems. It can be seen that NP has a greater influence on the base fluid atoms than the pure base fluid atoms. In the small NP system, H and O atoms are more likely to appear near Cu atoms. As the size of NP increases, the probability of finding H and O atoms on the surface of the NP decreases. The impact is greater than the large NP system. It can also be found that the peak of the radial distribution function of the Cu-O(a) atom pair is higher than that of the Cu-H(b) atom pair, which means that the probability of Cu atom finding an O atom around it is greater than that of finding H atoms around it. But since the number of H atoms in the base fluid is twice that of O atoms, the arrangement of H and O atoms around NP is different from that of the base fluid, and O atoms near NP is closer to NP and the H atom is slightly far away from NP (as shown in Figure 6), which means that the force between Cu and O atoms in the base fluid is higher than the force between Cu and H atoms.

Fig. 5 Radial distribution functions between O-Cu(a) and H-Cu(b) atom pairs in the three systems

Fig. 6 The arrangement of H and O atoms on the surface of nanoparticles
4. Conclusion:
(1) Nanoparticles of different sizes in the nanofluid have different effects on the base fluid, and the number density of base fluid atoms on the surface of different particles decreases as the size of the nanoparticles decreases;
(2) There is basically no change between the pure base liquid atoms in the nanofluid, and the nanoparticles have a greater influence on the base liquid atoms, and the smaller the nanoparticle size, the more attractive the base liquid atoms;
(3) The atomic arrangement of the base liquid around the nanoparticle is different from that of other places, and the O atom is closer to the nanoparticle than the H atom.

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