

Molecular Dynamics Study on the Contribution of Particle Surface Adsorption Layers to Nanofluid Thermal Conductivity (Postprint)

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Full Text

Molecular Dynamics Study of the Contribution of Particle Surface Adsorption Layers to the Thermal Conductivity of Nanofluids

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Abstract

This study employs equilibrium molecular dynamics simulations to investigate the thickness and structure of the adsorption layer surrounding solid nanoparticles in nanofluids, and calculates the thermal conductivity distribution within

this layer using the Green-Kubo formalism. The results demonstrate the existence of a 0.5 nm thick adsorption layer around nanoparticles, within which the atomic number density increases by 50–60% and the thermal conductivity enhances by 200–300%. Analysis reveals that the enhanced thermal conductivity arises from both the increased atomic number density and the higher degree of atomic ordering within the adsorption layer. These findings are expected to provide critical parameters and theoretical guidance for developing accurate predictive models of nanofluid thermal conductivity.

Keywords: nanofluid; adsorption layer; thermal conductivity; molecular dynamics

0 Introduction

Nanofluids represent a novel class of heat transfer and cooling media formed by dispersing nanoscale metallic or non-metallic solid particles into base liquids at specific concentrations [1]. Numerous experimental studies have shown that the addition of nanoparticles significantly enhances the thermal conductivity of nanofluids [2–6]. However, when classical models based on effective medium theory are applied to predict the thermal conductivity of these solid-liquid mixtures, they consistently underestimate the experimental values [7–9]. To address this discrepancy, researchers have proposed various heat transfer mechanisms based on nanoparticle characteristics, which can be summarized into three main categories: (1) Brownian motion of particles and the resulting micro-convection [10–14]; (2) particle aggregation [15–19]; and (3) liquid adsorption layers on particle surfaces [20–25].

In 2001, Choi [20] first proposed that an adsorption layer exists between nanoparticles and the base fluid, featuring higher atomic number density and more ordered atomic arrangement than the pure liquid, consequently exhibiting greater thermal conductivity. Building upon this theory, Yu and Choi [21,22] developed modified Maxwell and Hamilton-Crosser models. Subsequent work by Leong [23], Xie [24], and Rizvi [25] also incorporated particle surface adsorption layers to develop different predictive models. While some of these models show good agreement with certain experimental results, none can independently determine the two crucial parameters—adsorption layer thickness and thermal conductivity. Therefore, alternative methods are necessary to investigate adsorption layers. In 2009, Gerardi [26] used nuclear magnetic resonance experiments to measure a 1.4 nm thick liquid adsorption layer on alumina nanoparticle surfaces, though such experimental results remain scarce in the literature [27]. Conversely, at the nanoscale, the rapid development of molecular dynamics provides an effective tool for adsorption layer research [28–33]. This study employs equilibrium molecular dynamics for the first time to calculate the thermal conductivity distribution within the adsorption layer and analyzes the atomic number density distribution and factors influencing thermal conductivity in this region.

1 Simulation Method

Molecular dynamics serves as an effective approach for investigating nanofluid thermal conduction mechanisms from a microscopic perspective [27]. Starting from initial positions and velocities of each atom, molecular dynamics simulations apply Newtonian mechanics and interatomic potential functions to determine the forces on each atom, thereby obtaining their subsequent positions and velocities. This process yields the temporal evolution of every atom in the system, enabling the explanation of macroscopically observable physical properties from microscopic atomic motion.

In this work, we select argon (Ar) atoms as the base fluid and copper (Cu) or silver (Ag) atoms as the solid nanoparticles. The Ar potential function and parameters show excellent agreement with experimental values, making this nanofluid system widely adopted in various experimental and theoretical studies [28–33]. As shown in [Figure 1: see original paper], we first construct a cubic simulation box with a side length of 10 nm. A spherical region at the box center accommodates the nanoparticle, which is constrained within a spherical zone 0.1 nm larger than its radius to facilitate subsequent thermal conductivity calculations. Ar, Cu, and Ag atoms are arranged in a face-centered cubic (FCC) structure with lattice constants of 573.06 pm, 361.49 pm, and 407.30 pm, respectively. The Ar lattice constant is calculated based on a liquid argon density of 1410 kg/m³.

The L-J potential function is employed for Ar-Ar, Cu-Cu, and Ar-Cu atomic interactions, taking the form:

$$U(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad \text{for } r_{ij} \leq r_c$$

where r_{ij} is the distance between atoms i and j , r_c is the cutoff radius (taken as 1.5 nm), and ε and σ are the energy and length parameters of the potential function. Parameters for different atom types are obtained using the Lorentz-Berthelot mixing rules. The specific potential parameters used in this simulation, sourced from the literature, are listed in [32].

The simulation employs periodic boundary conditions with a time step of 0.1 fs. The system temperature is set at 85 K. The system runs for 2,000,000 steps in the NVT ensemble, followed by another 2,000,000 steps in the NVE ensemble to achieve full equilibrium. After recording the atomic populations in each region, thermal conductivity is calculated during a final 1,000,000 steps in the NVE ensemble.

According to the Green-Kubo formalism, thermal conductivity is obtained by integrating the autocorrelation function of microscopic heat flux:

$$\lambda = \frac{1}{3Vk_B^2} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$

where k_B is the Boltzmann constant, V is the volume of the calculation region, T is the system temperature, and \mathbf{J} is the microscopic heat flux of atoms in the calculation region, defined as:

$$\mathbf{J} = \frac{d}{dt} \sum_i e_i \mathbf{x}_i = \sum_i e_i \mathbf{v}_i + \frac{1}{2} \sum_{i,j} (\mathbf{f}_{ij} \cdot \mathbf{v}_i) \mathbf{x}_{ij}$$

where e_i is the total energy (potential plus kinetic) of atom i , \mathbf{v}_i is its velocity vector, \mathbf{f}_{ij} is the force between atoms i and j , and \mathbf{x}_{ij} is their separation vector.

2 Results and Discussion

2.1 Determination of Equilibrium State

Ensuring the system reaches equilibrium before calculating thermal conductivity is crucial. For systems with many atoms (e.g., 9,000), temperature or energy stabilizes quickly regardless of equilibrium status [32]. With over 20,000 atoms in our simulation system, temperature or energy fluctuations alone are insufficient to determine equilibrium. In molecular dynamics studies of nanofluid adsorption layers, the time evolution of atomic number density around solid particles serves as an effective equilibrium criterion [32].

As shown in [Figure 2: see original paper], temperature fluctuations become minimal after 500,000 steps (50 ps), at which point we begin our analysis. [Figure 3: see original paper] plots the radial distance from the nanoparticle surface against atomic number density n , calculated from the number of atoms N and volume V in each spherical shell region:

$$n = \frac{N}{V}$$

Comparing the density distributions at 50 ps and 100 ps reveals a substantial increase in atomic number density near the nanoparticle surface, indicating atomic migration toward the surface due to solid-liquid interactions and confirming the system has not reached equilibrium. In contrast, comparisons between 100 ps, 200 ps, 300 ps, and 400 ps show minimal fluctuations in density distribution, indicating the system achieves equilibrium by 400 ps.

After equilibration, thermal conductivity calculations proceed in the NVE ensemble. While the integration time in equation (3) should theoretically be infinite, practical constraints require finite computation times. However, excessively short integration times introduce significant errors. In equilibrium molecular dynamics calculations, appropriate integration times can be selected

based on the convergence of heat flux or thermal conductivity results [31]. As shown in [Figure 4: see original paper], thermal conductivity gradually converges to a constant value as integration time increases, with computational errors approaching zero. Selecting 100,000 steps (100 ps) as the integration time is therefore reasonable for this simulation.

2.2 Atomic Number Density Distribution

In molecular dynamics simulations, increased atomic number density around nanoparticles is used to characterize adsorption layers [32-34]. This study divides the region surrounding the nanoparticle into a series of adjacent spherical shells with 0.1 nm thickness and calculates the atomic number density in each region to obtain the density distribution. As shown in [Figure 5: see original paper], density peaks appear at 0.2 nm, 0.5 nm, and 0.8 nm, while beyond 0.8 nm the density becomes uniform and can be considered as that of pure liquid argon. Compared to the pure liquid argon density of 21 atoms/nm³, the average density in the 0-0.2 nm region is 46 atoms/nm³, and in the 0-0.5 nm region it is 29 atoms/nm³, indicating the formation of an approximately 0.5 nm thick adsorption layer around the nanoparticle. On average, this 0.5 nm thick adsorption layer exhibits a 50-60% increase in atomic number density.

Furthermore, [Figure 5: see original paper] shows that atomic number density at 0.1 nm and 0.3 nm is significantly lower than that of pure liquid argon, revealing highly non-uniform density distribution within the adsorption layer. This non-uniformity arises because adsorption layer formation depends not only on solid-liquid interactions but also on liquid-liquid interactions. As shown in [Figure 6: see original paper], in the 0-0.1 nm region, strong repulsive forces due to close proximity result in lower atomic density. In the 0.1-0.2 nm region, attractive solid-liquid interactions create a density maximum. In the 0.2-0.5 nm region, liquid-liquid interactions dominate. The extremely high density in the 0.1-0.2 nm region strengthens its influence on neighboring regions, exerting repulsive forces on atoms in the adjacent 0.2-0.3 nm region (causing a sharp density decrease) and attractive forces on atoms in the more distant 0.4-0.5 nm region (causing a density increase). Beyond 0.5 nm, solid-liquid interactions become negligible, and all density extrema can be explained through this interplay of forces.

Wang et al. [34] demonstrated that adsorption layers exhibit a double-layer structure similar to a diffuse electric double layer, with an inner layer thickness of approximately 0.42 nm and a total thickness of about 0.76 nm, which aligns with our findings. However, their work did not explore the underlying reasons for this structure in depth. In Cui et al.'s study [32], the overall downward trend in atomic number density curves over time indicated a decreasing total atom count, which is unreasonable given their use of periodic boundary conditions.

As nanoparticle diameter increases from 1 nm to 3 nm, neither the thickness nor structure of the adsorption layer shows significant changes. Comparing [Figure

7: see original paper] reveals that adsorption layer thickness and structure vary little with nanoparticle material.

2.3 Thermal Conductivity Distribution

Using equilibrium molecular dynamics based on the Green-Kubo formalism, we calculate the thermal conductivity of each spherical shell region after equilibration, obtaining the thermal conductivity distribution (excluding the 0–0.1 nm region). The results are presented in [Figure 8: see original paper] and [Figure 9: see original paper]. On average, thermal conductivity increases by 300–600% in the 0.1–0.2 nm region and by approximately 200–300% in the 0.1–0.5 nm region, demonstrating that thermal conductivity within the adsorption layer exceeds that of pure liquid argon.

Babaei et al. [31] showed that equilibrium and non-equilibrium molecular dynamics methods yield consistent thermal conductivity results for nanofluids, with negligible differences. However, Liang et al. [30] used non-equilibrium molecular dynamics to study Cu/Ar systems and reported only a ~60% increase in adsorption layer thermal conductivity, which differs significantly from our results. This discrepancy primarily stems from their selection of a 1.158 nm adsorption layer thickness. When we adopt a 1.1 nm thickness, our adsorption layer thermal conductivity increases by only 40–50%, which is lower than Liang's value. The main reason is that Liang's adsorption layer formed on a copper atomic wall rather than a spherical particle, resulting in a rectangular layered structure rather than a spherical shell geometry. Consequently, the volume of the high-conductivity 0.1–0.2 nm thin layer is substantially larger in their model, explaining the difference between their results and ours.

Comparing the atomic number density and thermal conductivity distributions reveals synchronized trends between corresponding curves in [Figure 5: see original paper] and [Figure 8: see original paper], as well as [Figure 7: see original paper] and [Figure 9: see original paper]. Density peaks at 0.2 nm, 0.5 nm, and 0.8 nm (and even 1.1 nm) correspond to thermal conductivity peaks, while density minima at 0.3 nm, 0.6 nm, and 0.9 nm correspond to thermal conductivity minima. Moreover, regions with higher atomic number density consistently exhibit higher thermal conductivity, and vice versa, indicating a close relationship between thermal conductivity enhancement and atomic number density.

To explore this relationship, we define a dimensionless atomic number density n^* as:

$$n^* = \frac{n}{n_0}$$

where n is the atomic number density in each spherical shell region and $n_0 = 21$ atoms/nm³ is the density of pure liquid argon. Using the ratio of thermal conductivity to dimensionless atomic number density to characterize each atom's contribution to thermal conductivity, we obtain [Figure 10: see original paper]

and [Figure 11: see original paper]. The results show that each adsorption layer atom' s contribution to thermal conductivity also increases significantly in the 0.1-0.5 nm region, by approximately 40-50% on average.

This analysis demonstrates that the formation of adsorption layers and their high thermal conductivity fundamentally result from strong solid-liquid interactions. These interactions increase the surrounding atomic number density while simultaneously enhancing the degree of atomic ordering, optimizing the thermal conduction structure and increasing each atom' s contribution to thermal conductivity.

3 Conclusions

This study investigates the distribution of atomic number density and thermal conductivity in adsorption layers using equilibrium molecular dynamics simulations. The main conclusions are:

- (1) Simulations reveal an adsorption layer thickness of approximately 0.5 nm. Compared to pure liquid, the atomic number density within this layer increases by 50-60%, while thermal conductivity enhances by 200-300%. These results provide theoretical support for accurately predicting nanofluid thermal conductivity.
- (2) Due to the interplay between solid-liquid and liquid-liquid atomic interactions, both atomic number density and thermal conductivity distributions within the adsorption layer are highly non-uniform. In our simulations, adsorption layer thickness does not vary significantly with nanoparticle size.
- (3) The enhanced thermal conductivity of adsorption layers results from both increased atomic number density and improved atomic ordering, with both factors contributing comparably.
- (4) Adsorption layer formation stems from solid-liquid interactions being stronger than internal liquid forces, suggesting that solid-liquid interaction strength should be considered when selecting nanofluids for practical applications.

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