Molecular dynamics simulations of thermal boundary resistances in a liquid between two solid walls separated by a nano gap ☆

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ARTICLE INFO

ABSTRACT

Molecular dynamics simulations are performed to study heat conduction in a liquid argon between two copper walls separated at a nano distance. Effects of wall wettabilities and separation distances on thermal boundary resistances of two solid–liquid interfaces at a constant heat flux are obtained. Simulation results show that the thermal boundary resistance consists of two parts in series: (i) the resistance between solid walls and the nanolayer absorbed on it, and (ii) the resistance between the nanolayer and bulk liquid or the other nanolayer if there is no bulk liquid in between. While the first part of thermal boundary resistance has already been widely studied, the second part is often overlook which is the subject of discussion in this paper. When the solid wall becomes more and more hydrophilic, the first part decreases while the second part has the opposite trend which leads to a minimum thermal boundary resistance. The increase of the second part of resistance with increasing wall wettability can be explained by: (i) larger differences in vibrational densities of states (VDOSs) of the nanolayer and the bulk liquid, which indicates that atoms in both sides are more difficult to be in resonance, leading to weaker heat conduction and (ii) less atom exchange between the nanolayer and liquid atoms bulk liquid or the other nanolayer, leading to less atomic energy exchange between the nanolayer and bulk liquid. With the separation distance becoming larger, the thermal boundary resistance increases at first and then approaches a constant value asymptotically.

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1. Introduction

With rapid advances in nanotechnology, the size of Micro-Electro-Mechanical Systems becomes smaller and smaller. In such microsystems, the specific surface area is large and surface effects cannot be ignored [1]. The solid–liquid thermal boundary resistance (i.e. the well-known Kapitza resistance) has been studied theoretically and experimentally to explain the temperature drop on the interface between two different materials in a thermal transport process [2–4]. Molecular dynamics (MD) simulation has been widely used to explore the relationship between interatomic interactions and thermal boundary resistance. Based on molecular dynamics simulation results, Shenogina et al. [5] obtained a correlation in which he found a linear relationship between thermal boundary conductivity and cosine of contact angle of the solid wall. Many previous MD studies [3,4,6] found that liquid atoms near a solid wall can be absorbed on the wall to form a nanolayer with a thickness of a few atoms, which is closely related to solid–liquid thermal boundary resistance. Generally, the more hydrophilic is the solid wall, the more regular the nanolayer will be formed, leading to lower thermal

boundary resistance. However, the role of nanolayer in the heat transfer process through an interface remains unknown. Lin et al. [7] believed that the existence of the nanolayer enhanced heat transfer process at the solid–liquid interface whereas Xue et al. [8] did not agree with this conclusion. Thus, more studies are needed to reveal the effect of nanolayer on the thermal boundary resistance. Recently, Liang and Tsai [9] carried out a molecular dynamics simulation on a nano gap which is filled with a few liquid atoms between two solid walls to study the effect of liquid film thickness on the thermal resistance. They found that there was a very small thermal resistance when only one layer of molecular layer exists between two walls. In addition, when the wall separation distance becomes larger, a dramatic increase in thermal boundary resistance was found, which was explained by the larger differences of vibrational density of states between solid walls and the nanolayer as the wall separation distance was increased. However, they did not explain why the solid–liquid thermal boundary resistance increased only slightly when the wall separation distance was increased further.

Inspired by Liang and Tsai's [9] work, we carry out a molecular dynamics simulation on a similar system where a small quantity of liquid argon atoms is placed between two copper solid walls separated by a distance of several nanometers in this paper. With such a system, we study the solid–liquid interface structure and the constituent of thermal boundary resistance. Effects of the nanolayer on the solid–liquid thermal boundary resistance under different wettabilities and wall distances

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are studied. Finally, the vibrational density of states of nanolayer and bulk liquid and atom number in the nanolayer are analyzed to explain the phenomena.

2. Simulation method

The 12-6 Lennard–Jones potential function is employed to describe the interaction between atoms:

$$U_{ij}(r_{ij}) = 4\varepsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right) \tag{1}$$

where r_{ij} is interatomic spacing between atoms i and j while σ and ε are parameters to describe the bonding balance distance and bonding energy respectively. The parameters to describe interaction between argon and copper atoms can be obtained by Lorentz–Berthelot mixing rules [10]:

$$\begin{cases} \varepsilon_{ls} = \mu\sqrt{\varepsilon_l\varepsilon_s} \\ \sigma_{ls} = \dfrac{\sigma_l + \sigma_s}{2} \end{cases} \tag{2}$$

where μ is a parameter related to the interaction strength between solid and liquid. A larger μ leads to stronger interaction strength between solid and liquid resulting in a more hydrophilic wall [11–14]. Maruyama et al. pointed out a liner relationship between cosine of contact angle and solid–liquid atomic interaction parameter ε_{ls}. When ε_l and ε_s are constant, it can be shown that:

$$\cos\theta \propto \mu \tag{3}$$

where θ is the contact angle. Nine values of $\mu = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8$ are used in our simulation to study the effect of solid–liquid interaction at the solid–liquid interface, respectively. Table 1 lists the parameters in the potential function given by Eq. (1) for different atomic interactions.

Fig. 1 shows the simulation system containing a slab of liquid argon bounded by two copper walls. The lattice constant number of Cu is $a_0 = 0.361$ nm. The size of the simulation domain is $15a_0 \times (N + 12)a_0 \times 15a_0$ in x-, y- and z-directions respectively, where Na_0 represents the wall separation distances in the y-direction, and N can be any number and we use $N = 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5$ in this paper to indicate the increasing wall separation distance. It follows that the thickness of liquid argon slab in the y-direction is also Na_0. Both ends of the system in the y-direction are fixed. The atoms in the fixed layers are kept motionless to ensure that the volume of simulation system remains unchanged through the entire simulation process. A heat source is placed on the left of the simulation system and a heat sink is placed on the right symmetrically, making heat flow from left to right in the direction perpendicular to solid–liquid interfaces. Periodic boundary conditions are applied to x- and z-directions and non-periodic boundary conditions are applied in the y-direction. Time step is set to be 1 fs and cutoff radius for all interactions is 0.8 nm.

Before the simulation for heat conduction process between the heat source and heat sink is carried out, the number of liquid atom placed in the gap in different wall separation distances with different solid–liquid atomic interactions must be computed as the initial conditions. In order

Table 1
Values of atomic interaction parameters [15] in Eq. (1) used for simulations.

Interaction	$\varepsilon(\times 10^{-21}\text{J})$	$\sigma(nm)$
Cu—Cu	1.67	0.3405
Ar—Ar	65.63	0.2338
Cu—Ar	10.42μ	0.2872

to be comparable under different wettabilities and separate distances, the initial conditions of the liquid argon must be the same. To this end, computation is first carried out for an open system as shown in Fig. 1(b), where the liquid argon (indicated by blue) is allowed to move freely to the reservoir. We choose the initial condition of liquid argon at 200 K at a density of 1.4 kg/L (i.e., at 1 atmospheric pressure) in Fig. 1(b). This system of Fig. 1(b) has the same wall wettability and separation distance as in Fig. 1(a). The system is heated to an average temperature of 200 K and then run 30,000 time steps to reach a steady state. The atom number of the liquid argon in the square region ($15a_0 \times 15a_0$) bounded by dash lines in Fig. 1(b) is used as the initial liquid argon atom number of the system in Fig. 1(a).

After the initial liquid atom number is determined, the whole simulation system, as shown in Fig. 1(a), is heated with Nose–Hoover thermostat in the canonical ensemble (NVT) for 15,000 time steps and then run with a microcanonical ensemble for 25,000 time steps to ensure the system in a uniform temperature of 200 K as the initial condition. Then, a heat source (with kinetic energy supplied) is placed on the left side of the copper wall and a heat sink is placed on the right side of the copper wall by subtracting the same amount of kinetic energy at every two time steps. In this way, a steady temperature gradient from the heat source to the heat sink can be maintained while the total energy of the system is conserved. When $N > 1.0$, a heat flux of $q = 1.09$ GW/m² is imposed, and when $N = 1.0$, a larger heat flux of $q = 2.18$ GW/m² is imposed (otherwise, the temperature gradient would be too small to calculate if $q = 1.09$ GW/m² is imposed). With the above method, a simulation for $N = 15.0$ is first carried out and the thermal conductivity of the liquid argon is obtained from heat flux divided by the temperature gradient in the liquid argon $3a_0$ away from both walls. Results of this MD computation show $\lambda = 0.140$ W/(K·m), which is in excellent agreement with experimental data [16] of 0.141 W/(K·m) for liquid argon at a temperature of 200 K and a density of 1.4 kg/L. This confirms that our molecular dynamics simulation is reliable and accurate.

3. Results and discussion

The thermal boundary resistance (i.e. Kapitza resistance) can be expressed by $R_k = \Delta T / q$, where ΔT is the temperature drop at the interface and q is the heat flux across the interface. The total thermal resistance R is defined as:

$$R = \frac{\Delta T_w}{q} \tag{4}$$

where ΔT_w is the temperature difference of two walls obtained from simulation. On the other hand, R is also given by

$$R = R_{k1} + R_{liquid} + R_{k2} \tag{5}$$

where R_{k1} and R_{k2} are liquid thermal boundary resistances of the two solid–liquid interfaces, and R_{liquid} is the heat-conduction resistance of the liquid argon. Substituting Eq. (3) into Eq. (4) to give the total thermal boundary resistance (i.e., the sum of the two thermal boundary resistances at the solid–liquid interfaces) as:

$$R_k = R_{k1} + R_{k2} = \frac{\Delta T_w}{q} - R_{liquid}. \tag{6}$$

3.1. Effects of different wettabilities and wall separation distances

The numbers ①, ② and ③ in Fig. 2 indicate the wall, the nanolayer and the bulk liquid respectively, and snapshots of atoms in the liquid argon between two solid Cu walls with the same wettability of $\mu = 1.0$ are presented. Note that the curves in Fig. 2 start from y =