A Molecular Dynamics Study on the Effects of Nanostructural Clearances on Thermal Resistance at a Liquid Water-Solid Interface

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Abstract. The classical molecular dynamics simulation was conducted in order to clarify the effects of surface structural clearances at the nanometer scale on thermal resistance at a liquid water-solid interface as well as static and dynamic behaviours of fluid molecules in the vicinity of the surface. A liquid molecular region confined between two solid walls, of which the interparticle potential was Lennard-Jones type or SPC/E type, was employed as a calculation system. The thermal resistance between the liquid molecular region and the solid walls with nanostructures was calculated by the heat flux and the temperature discontinuity obtained in the molecular dynamics simulations. With changing the surface structural clearances and the potential energy functions the thermal resistance at the interface once decreased and got to the minimum value when the structural clearances were changed from 0 to several nm.

1. Introduction
Due to ongoing progress in material surface treatments and in nano/micro scale processing, it is feasible to fabricate various structures at nano- or micrometer scale on a solid surface. On the other hand, the molecular dynamics method has been applied to understand static structures and transport phenomena at the molecular scale at a liquid-solid interface, and a substantial thermal resistance was found at the liquid-solid interface, as well as between solid-solid interfaces when observed at the molecular scale [1-7]. The authors have previously reported that there was some energy transfer difference at a liquid-solid interface depending on surface structures and structural clearances at the nanometer scale when we observe the energy transfer at the interface [8-11]. Effects of surface structures and structural clearances at the nanometer scale on the interfacial thermal resistance between liquid and solid were also discussed from the molecular dynamics point of view [12-13]. In the present study a liquid molecular region confined between the solid walls, of which the intermolecular potential was Lennard-Jones type or SPC/E type, was employed as a calculation system. The temperature of the middle layers of the upper and the lower solid walls were controlled by the Langevin method [14,15] in order to make a temperature gradient in the calculation system. Effects of surface structures and surface structural clearances on the thermal resistance between liquid and solid as well as static structures and dynamic behaviours of fluid molecules were investigated directly by the classical molecular dynamics method.

2. Numerical methods
Figure 1 shows one of calculation models employed in the present study and it shows surface structures at the nanometer scale and snapshots in liquid molecular region too. A liquid molecular region of which the size was $2.8 \times 2.8 \times 2.8 \, \text{nm}^3$ or $5.6 \times 5.6 \times 5.7 \, \text{nm}^3$ was confined with upper and lower solid walls as a unit cell. Periodic boundary conditions were employed in $x$ and $y$ directions. Upper and lower solid walls consisted of three solid layers where the outermost layers were fixed and the temperatures of the middle layers were controlled at constant by the Langevin method. We assumed that there were various nanostructures of $0.7 \, \text{nm}$ height attached to the lower solid wall and the structural clearances were changed from $0.00$ to $2.81 \, \text{nm}$. As shown Fig. 1 the nanostructures attached to the surface have the periodic groove structures in $y$ direction. When the initial surface structural clearance was less than $0.4 \, \text{nm}$ in case of surface (b) in Fig. 1, the surface nanostructures were so small that they were broken down into random structures. Nanostructures in the unit cell consisted of the same number of atoms. Density in the liquid molecular region was kept constant and the effects of liquid density on the thermal resistance were already discussed in the previous study [12]. The temperature gradients were formed in the liquid molecular region by controlling the temperatures of the upper wall $T_i$ and the lower walls $T_h$, respectively. The difference between $T_i$ and $T_h$ was adjusted to about $50\, \text{K}$ in the present study. The numerical uncertainty of the temperature and the temperature gradient obtained was directly dependent on the total calculation time and it was within $5\%$ in the present calculation time. The 12-6 Lennard-Jones potential energy functions and SPC/E potential functions with cutoff distances were employed in the present study so as to understand the energy transfer phenomena qualitatively. The 12-6 Lennard-Jones potential parameters of liquid molecules correspond to those of water molecules and potential parameters of the wall atoms correspond to those of iron atoms. We employed the 12-6 Lennard-Jones potential functions and the SPC/E potential functions with cut off distances for the rigid water molecules [16,17] so as to investigate the effects of the potential functions between liquid molecules on the calculated thermal resistance. Temperature gradients and energy transfer at upper and lower walls were calculated numerically after a relaxation calculation of $1.0 \, \text{ns}$. Newton’s equations were integrated numerically by the Verlet method with a time interval of $5 \, \text{fs}$ for Lennard-Jones water models and $0.1 \, \text{fs}$ for SPC/E water models.
respectively. The thermal resistance $R_t$ between a solid wall and a liquid region was calculated by the following equations as,

$$R_t = \frac{\Delta T}{Q},$$

where $\Delta T$ is the temperature discontinuity between the solid wall and the liquid region and $Q$ is the energy flux that was added or subtracted by the Langevin method per unit area (divided by the unit cell size in x-y plane) so as to control the solid wall temperature at constant. We can obtain a certain temperature gradient in the liquid region as well as in the solid walls during a molecular dynamics simulation. By using the temperature gradient obtained by the molecular dynamics simulation we can calculate the temperature discontinuity $\Delta T$ between the solid wall and the liquid region as a result. The energy flux in the calculation domain $Q$ can be calculated by the energy input at the lower wall (heating wall). We checked that the energy output at the upper wall (cooling wall) exactly coincided with the energy input at the lower wall. The similar calculation method of the thermal resistance was employed in the molecular dynamics simulations and reported by Maruyama et al. [3,4] and the similar calculation method of the temperature gradients was also applied in the molecular dynamics simulation and reported by Ohara et al. [5,6].

3. Calculation results

3.1 Effects of Nanostructural Clearances on Thermal Resistance Depending on Degrees of Freedom of Water Molecules

Figure 2 shows effects of the nanostructural clearances on the thermal resistances calculated by rotational temperature, translational temperature and the average temperature when the intermolecular potential functions are the SPC/E potential with cut off distance $r_c=1.3$nm. The rotational temperature $T^{rot}$, the translational temperature $T^{trans}$ and the average temperature $T^{ave}$ can be calculated by the following equations,
where \( r_v \), \( v_i \), \( N \), \( m \), \( v \), \( I \) and \( \omega \) are rotational degrees of freedom, translational degrees of freedom, number of water molecules, mass of a water molecule, translational velocity, moment of inertia and angular velocity, respectively. The nanostructural clearances \( L \) are changed as 0.00, 0.35, 0.70 and 1.40 nm. Figure 3 shows the gradients of translational temperature and rotational temperature depending on the surface nanostructural clearances. All thermal resistances calculated by the translational temperature, the rotational temperature and the average temperature of water molecules once decreased and got to the minimum value and increased again with the increase of the nanostructural clearances and the order of the calculated thermal resistances was in the range from 1.5×10^{-9} to 3×10^{-9} m^2K/W. The thermal resistance calculated by the rotational temperature was larger than that by the translational temperature under the condition of the same nanostructural clearance. In the case of \( L = 0.00 \) nm, in other words a flat surface, the thermal resistance calculated by the translational temperature coincided with that by the rotational temperature. Hence, the thermal resistance differences depending on degrees of freedom of water molecules, the translational and rotational temperature, came from the interaction between the nanostructural clearances and the water molecular dynamic motions. The rotational motions of water molecules in the nanostructural clearances were somewhat restricted although the effective surface area in the molecular scale was enlarged by the nanostructures.

### 3.2 Effects of Nanostructural Clearances on Thermal Resistance Depending on Potential Energy Functions between Water Molecules

Figure 4 shows the effects of the nanostructural clearances and the potential energy functions between water molecules on the thermal resistances at a liquid water-solid interface. Potential energy functions
between water molecules employed in the present study were 12-6 Lennard-Jones potential function and SPC/E potential function with the cut off distance \( r_c = 1.3 \) nm. In the case of SPC/E potential the thermal resistances were calculated by the average temperature of translational and rotational temperature of water molecules. Regardless of the potential energy functions between water molecules and the nanostructural clearances the order of the thermal resistances calculated was in the range from \( 1.5 \times 10^{-9} \) to \( 4.5 \times 10^{-9} \) m\(^2\) K/W. The thermal resistances calculated once decreased and got to the minimum value and increased again in both cases of the potential energy functions. The thermal resistances with nanostructures were lower than those of flat surface in the cases of both potential functions. The thermal resistance at a liquid water-solid interface has much relationship with the surface area enlargement and the mobility change of water molecules depending on the nanostructural clearances.

4. Conclusions
The classical molecular dynamics simulation was conducted in order to clarify effects of surface structural clearances at the nanometer scale and potential energy functions on a thermal resistance at a liquid water-solid interface. A liquid molecular region confined between two solid walls, of which the intermolecular potential was Lennard-Jones type or SPC/E type, was employed as a calculation system. A thermal resistance at a liquid water-solid interface with nanostructures was calculated by the heat flux and the temperature discontinuity obtained by the molecular dynamics simulation. The surface structures and the structural clearances were changed as calculation parameters. The main findings were as follows:
(1) There was a certain difference between the thermal resistance calculated by the translational temperature and that by the rotational temperature depending on the interfacial structural clearances when the SPC/E potential functions were employed as the intermolecular potential functions between water molecules.
(2) The thermal resistance at the liquid water-solid interface passed through a minimum value when the interfacial structural clearances were changed at the nanometer scale.

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