The effects of the structural geometry at the nanometer scale on the thermal resistance at a liquid molecule-solid interface, as well as the interfacial energy transport mechanism of liquid molecules, were investigated directly by the nonequilibrium classical molecular dynamics simulations. The 12-6 Lennard-Jones potential energy functions for liquid molecules and the channel structure at the nanometer scale are employed so as to discuss the effects of the surface geometry at the nanometer scale on the interfacial thermal resistance in comparison with a flat surface. The thermal resistance between solid and liquid molecules was calculated by the temperature discontinuity at the liquid-solid interface and the energy flux that was added or subtracted by the Langevin method per unit area so as to maintain a constant boundary temperature of solid walls. The substantial interfacial thermal resistance reduction depending on the interaction parameters between solids and liquid molecules was observed in the case of the nanostructure surface in comparison with the flat surface. The liquid-solid interfacial thermal resistance reduction in the case of nanostructure surface relates to the energy transport mechanism change at the liquid-solid interface and the surface area magnification.

**Key words:** Thermal Resistance, Liquid-Solid Interface, Surface Nanostructural Geometry, Energy Transport Mechanism, Nonequilibrium Molecular Dynamics Simulation

1. Nomenclature

\[ A_{2f} \] : the ratio of energy transport through molecular interactions to the total energy transport in case of flat surface

\[ A_{2n} \] : the ratio of energy transport through molecular interactions to the total energy transport in case of nanostructure surface

\[ \alpha \] : interaction parameters between solid and liquid molecules

\[ E_i \] : total energy of molecule \( i \) \( \text{J} \)

\[ \varepsilon \] : Lennard-Jones potential parameter \( \text{J} \)

\[ \varepsilon_{sl} \] : standard Lennard-Jones potential parameter between solid atoms and liquid molecules \( \text{J} \)

\[ F_{ij} \] : force vector between molecule \( i \) and molecule \( j \) \( \text{kg m/s}^2 \)
2. 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 in 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 [1-10]. One of the authors has previously reported studies of the energy transfer between liquid and solid at the molecular scale, and observed an energy transfer difference at the liquid-solid interface depending on the surface structures and the structural clearances at nanometer length scales [11-14]. The effects of the surface structures and the nanoscale structural clearances on the interfacial thermal resistance at the liquid-solid interface were also discussed from a molecular dynamics point of view by employing a Lennard-Jones potential or a SPC/E potential for the liquid molecules [15-19]. In the present study the modelled system consists of a liquid molecular region, employing 12-6 Lennard-Jones potential functions, confined between upper and lower solid walls. The temperature of the upper and the lower solid walls were held constant by the Langevin method [20-21] in order to produce a temperature gradient in the modelled system. The effects of the surface structures at the nanometer scale and the interaction parameters between solid and liquid molecules on the thermal resistance at a liquid-solid interface, as well as the interfacial energy transport mechanism at the molecular scale were investigated directly by the nonequilibrium classical molecular dynamics simulations.

3. Numerical Methods

Figures 1 (a) and (b) show the calculation models of the flat surface and the nanostructure surface employed in the present study, respectively, including a liquid molecular region confined between two solid walls. A liquid molecular region of size
2.8×2.8×5.7 nm³, confined by the upper and lower solid walls, was defined as a unit cell for the molecular dynamic simulation. Periodic boundary conditions were employed in the x and y directions as defined in Figures 1. The upper and lower solid walls consisted of six atomic layers where the outermost layers were fixed and the temperatures of the second layers from the outermost layers in the upper and lower solid walls were held constant by the Langevin method. The control volumes 1-10 shown in Figures 1 are defined in order to calculate the energy transport mechanism at the molecular scale numerically. The liquid-solid interface of the flat surface was defined as the plane parallel to two solid walls at the top position of the lower solid wall, the bottom of the control volume 1. On the other hand, the liquid-solid interface of the nanostructure surface is defined as the top of the control volume 1 in Figure 1 (b) and the interfacial thermal resistance was obtained by the average of temperature discontinuity between solid atoms and liquid molecules at the bottom of the control volume 1 and that at the top of the control volume 1. When we discuss the interfacial energy transport mechanism and the interfacial liquid density, the control volume just above the interface is employed. Hence, the control volume 1 and 2 are employed as the interfacial control volumes for the flat surface and the nanostructure surface, respectively.

In the present study the structural clearance L was defined as the periodic distance between nanostructures on the solid wall as shown in Figure 1 (b). We assumed that there were square channels of 0.70 nm depth and width attached to the lower solid wall and the structural clearances L=0.70 nm are employed. As shown in Figure 1 (b) the nanostructures attached to the surface formed the periodic channel structures in y direction. Total density in the liquid molecular region was kept constant at 1.21*10³ kg/m³; the effects of total liquid density in a control volume on the interfacial thermal resistance were discussed in a previous study [16]. Judging from the density and the average temperature of the system, the model liquid molecules remained in the liquid phase. The temperature gradients were formed in the liquid molecular region by controlling the temperatures of the lower and upper walls to be \( T_a = 355 \) K and \( T_b = 305 \) K, respectively. The numerical uncertainty of the temperature and the temperature gradient obtained was directly dependent on the total calculation time, which was set to be 3 ns after the relaxation calculation of 2 ns in the present study.

The 12-6 Lennard-Jones potential energy parameters shown in Table 1 were employed in the present study so as to understand the energy transfer mechanism for the simple shaped liquid molecules which have three degrees of freedom qualitatively. The Lennard-Jones potential parameters and mass of the liquid molecules and the wall atoms correspond to those of water molecules and iron atoms. The interaction between liquid
molecules and the wall atoms was described by the Lennard-Jones 12-6 potential function, the standard parameters $\sigma_{sl}$ and $\varepsilon_{sl}$ which were determined by the Lorentz-Berthelot combination rules. The potential parameter between liquid molecules and solid atoms $\alpha$ is expressed as the relative value, to the standard value and $\alpha$ is changed from 0.24 to 2.00 as shown in Table 1. Hence, the potential energy between liquid molecules and the solid atoms $\Phi_{sl}$ can be written as follows,

$$\Phi_{sl} = 4\alpha\varepsilon_{sl}\left[\left(\frac{\sigma_{sl}}{r}\right)^{12} - \left(\frac{\sigma_{sl}}{r}\right)^{6}\right],$$  \hspace{1cm} (1)

where $r$ is the distance between particles.

The temperature gradients and the heat flux through the upper and lower walls were calculated numerically after the relaxation calculation of 2 ns. Newton’s equations for solid atoms and liquid molecules were integrated numerically by the Leap Frog method. The thermal resistance between the solid wall and the liquid region $R$ was calculated by

$$R = \frac{\Delta T}{Q_z},$$  \hspace{1cm} (2)

where $\Delta T$ is the temperature discontinuity between the solid wall and the liquid region and $Q_z$ is the energy flux in z direction 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 maintain a constant solid wall temperature. In the present study the surface area magnification by the nanostructures was not considered for the calculation of the energy flux $Q_z$. 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 at the interfacial plane parallel to the upper wall. The energy flux in z direction $Q_z$ can be calculated by the energy input or output at the lower wall (heating wall) or at the upper wall (cooling wall). A similar nonequilibrium calculation method of the interfacial thermal resistance was employed in the nonequilibrium molecular dynamics simulations [2, 3, 4].

### 4. Calculation Results and Discussions

#### 4.1 Effects of the Surface Structure and the Interaction Parameters between Solid and Liquid Molecules on the Interfacial Thermal Resistances

Figure 2 shows the effects of the surface structure and the interaction potential energy parameters between solid and liquid molecules $\alpha$ on the thermal resistance at the liquid-solid interface. In the case of the flat surface the interfacial thermal resistance $R_f$

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{nm}$</th>
<th>$\varepsilon/10^{-21}$ J</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L - L</td>
<td>0.2641</td>
<td>5.59</td>
<td></td>
</tr>
<tr>
<td>S - S</td>
<td>0.2209</td>
<td>40.00</td>
<td></td>
</tr>
<tr>
<td>L - S</td>
<td>0.2425</td>
<td>3.59</td>
<td>0.24</td>
</tr>
<tr>
<td>L - S</td>
<td>0.2425</td>
<td>7.19</td>
<td>0.48</td>
</tr>
<tr>
<td>L - S</td>
<td>0.2425</td>
<td>14.95</td>
<td>1.00</td>
</tr>
<tr>
<td>L - S</td>
<td>0.2425</td>
<td>29.89</td>
<td>2.00</td>
</tr>
</tbody>
</table>

L: liquid molecules, S: solid atoms

Table 1  Lennard-Jones potential parameters.
decreases with the increase of the interaction parameter $\alpha$ and that at $\alpha = 0.24$ is about 4 times as large as that $\alpha = 2.00$. In the case of the nanostructure surface the interfacial thermal resistance $R_n$ decreases with the increase of the interaction parameter $\alpha$ when $\alpha$ is under 1.00 and $R_n$ increases again when $\alpha$ is over 1.00. The interfacial thermal resistance in the case of the nanostructure surface is less than that in the case of the flat surface when $\alpha$ is under 1.00 and the difference between them becomes very little when $\alpha$ is 2.00.

The interaction potential energy parameters between solid and liquid molecules $\alpha$ might have relationships with the interfacial local density of liquid molecules. Therefore, the relative interfacial density $\rho^*$ is defined and calculated by dividing the average density of liquid molecules in the interfacial control volume by that in the neighbouring control volume in the bulk direction. Concretely, $\rho_1/\rho_2$ for the flat surface and $\rho_2/\rho_3$ for the nanostructure surface are calculated and shown in Figure 3 and the subscript denotes the number of the control volume in Figures 1. The calculated interfacial local density of liquid molecules is dependent on the control volume size and the control volume size for the liquid density calculation is just equal to that for the temperature calculation in the present study. In the case of the flat surface the liquid molecular density at the solid-liquid interface increases with the increase of the interaction potential parameters between solid and liquid molecules $\alpha$. On the other hand, that is almost unity in the case of the nanostructure surface regardless of $\alpha$. The difference between the interfacial density in the case of the flat surface and that in the case of the nanostructure seems to have a relationship with the reduction of the interfacial thermal resistance in the case of the nanostructure surface when $\alpha$ is 0.24, in other words, the relative interfacial density is less than unity. However, the interfacial density difference doesn't seem to have much relationship with the interfacial thermal
resistance reduction in the case of the nanostructure surface when the relative density at the interface is over unity in the case of the flat surface. In order to discuss the variation of the thermal resistance at the liquid-solid interface depending on the surface geometry at the nanometer length scale as well as the interaction parameters between solid and liquid molecules $\alpha$ the energy transport mechanism at the molecular scale is investigated in the following section.

4.2 Effects of the Surface Structure and the Interaction Parameters between Solid and Liquid Molecules on the Interfacial Energy Transport Mechanism

The energy flux in $z$ direction $Q_z$ at the molecular scale can be written as [2],

$$Q_zV = \sum_i E_i v_{z,i} + \frac{1}{2} \sum_j z_{ij} v_{ij} \cdot F_{ij},$$

(3) where the first term on the right side is the energy transport through the molecular motions and the second term is the energy transport through the molecular interactions. The control volumes 1-10 in Figures 1 are used for the energy transport mechanism calculation at the molecular scale in Equation (3). The ratio of the energy transport through the first term on the right side in Equation (3) and that through the second term to the total energy transport in a control volume are calculated numerically and averaged during 3 ns.

The effects of the surface structure and the interaction parameters between solid and liquid molecules $\alpha$ on the ratios of the energy transport mechanism are shown in Figures 4 (1)-(4). When the interaction parameter $\alpha$ is 0.24 in the case of the flat surface, the energy transport ratio through the first term on the right side in Equation (3) in the control volume at the solid-liquid interface becomes larger than that in the bulk region. When the interaction parameter $\alpha$ is 0.48, 1.00 and 2.00 in the case of the flat surface, the energy transport ratio through the first term in the control volume at the solid-liquid interface is smaller than that in the bulk region. On the other hand, the energy transport ratio through the first term in Equation (3) at the solid-liquid interface is not so much different from that in the bulk region in the case of the nanostructure surface.

Figures 4 Effects of the surface structure and the interaction parameters between solid and liquid molecules $\alpha$ on the energy transport mechanism in the heat conduction direction.
Figure 5 shows the effects of the surface structure and the interaction parameters $\alpha$ on the interfacial energy transport ratio through the second term on the right side in Equation (3) and the ratios are denoted as $A_{2f}$ for the flat surface and $A_{2n}$ for the nanostructure surface. The ratio of the interfacial energy transport through molecular interactions, is smaller in the case of the flat surface than that in the case of the nanostructure surface when the interaction parameter $\alpha$ is 0.24.

Figure 6 shows the effects of the interaction parameter $\alpha$ on the difference between $A_{2f}$ and $A_{2n}$ and the ratio of the interfacial thermal resistance $R_n / R_f$. When the interaction parameter $\alpha$ is 0.24, the energy transport ratio through molecular interaction in the case of the flat surface $A_{2f}$ is about 0.08 smaller than that in the case of the nanostructure surface $A_{2n}$. When the interaction parameter $\alpha$ is 0.48, 1.00 and 2.00, the difference between $A_{2f}$ and $A_{2n}$ is smaller than that in the case of $\alpha = 0.24$. The surface area of the nanostructure surface employed in the present study is twice as large as that of the flat surface. $S^*$ denotes the surface area ratio of the nanostructure surface to the flat surface and $S^*$ is equal to 2.00 in the present study. As shown in the previous report [19] the area ratio $S^*$ has a relationship with the ratio of the interfacial thermal resistance $R_n / R_f$ and there are some differences between them depending on the interaction potential energy parameters between solid and liquid molecules $\alpha$. When the interaction parameter $\alpha$ is 0.24 or 1.00, the ratio of the interfacial thermal resistance $R_n / R_f$ is less than the inverse of the relative surface area $1/S^* = 0.5$ and $A_{2f}$ is smaller than $A_{2n}$ as shown in Figure 6. When the interaction parameter $\alpha$ is 0.48, the ratio of the interfacial thermal resistance $R_n / R_f$ is equal to the inverse of the relative surface area $1/S^* = 0.5$ and the difference $A_{2f}$ and $A_{2n}$ is relatively small as shown in Figure 6. In the case of $\alpha = 2.00$ the ratio of the interfacial
thermal resistance $R_n / R_f$ is almost unity and far from $1/S^* = 0.5$ because the surface adhesions of liquid molecules are observed and the relative surface area $S^*=2.00$ is not appropriate in this case. The increase of the energy transport through molecular interactions relates to the reduction of the interfacial thermal resistance ratio $R_n / R_f$ over the surface area magnification when $\alpha$ is relatively small. Hence, the difference of the interfacial energy transport mechanism as well as the surface area ratio $S^*$ have relations to the ratio of the interfacial thermal resistance $R_n / R_f$ when the interaction parameter between solids and liquid molecules $\alpha$ is relatively small.

5. Conclusions

Nonequilibrium classical molecular dynamics simulations were conducted in order to clarify the effects of the surface structural geometry at the nanometer scale and the potential parameters between solid and liquid molecules on the interfacial thermal resistance at the liquid-solid interface as well as the energy transport mechanism at the molecular scale in comparison with a flat surface. A liquid molecular region confined between the solid walls, of which the intermolecular potential was 12-6 Lennard-Jones type, was employed as the modelled system. The thermal resistance at the liquid-solid interface was calculated by the energy flux and the temperature discontinuity obtained in the nonequilibrium molecular dynamics simulations. The potential parameters between solid and liquid molecules are expressed as the relative value $\alpha$ to the standard value determined by the Lorentz-Berthelot combination rule. The surface with the periodic square channels of 0.70 nm height and width is employed as the structure surface.

The thermal resistance and the energy transport mechanism at a liquid-solid interface are dependent on the interfacial nanostructural geometry and the interaction parameters between solid and liquid molecules. The difference between the thermal resistance of the flat surface and that of the nanostructure surface relates to the change of the interfacial energy transport mechanism as well as the surface area magnification in comparison with the flat surface when the interaction parameter between solid and liquid molecules is relatively small.

References


