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SPECTRAL ANALYSIS ON HEAT TRANSFER BETWEEN LIQUID AND STRUCTURED SURFACE BASED ON MOLECULAR DYNAMICS

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ABSTRACT Heat transfer across solid-liquid interfaces at the nanometer scale is the important phenomenon in thermal science and engineering. This study examined effects of structures at the atomic scale on heat transfer mechanisms at a solid-liquid interface, using molecular dynamics simulations. As the structures, we adopted the attached atoms: adsorbed or clustered atoms on a flat solid surface, and the thermal transport and interfacial thermal resistance were investigated in detail. The results revealed the enhancement of the thermal transport is remarkable, that is, the thermal resistance is low, for the surface with the adsorbed atoms. The simulations also investigated the thermal transport mechanism from a spectral point of view focusing on the heat flux across the solid-liquid interface. The relationship between the thermal transport and the spectral heat flux was discussed, and the results showed that the thermal transport with the low frequencies is dominant in the case of the surface with the adsorbed atoms.

NOMENCLATURE

A	Interfacial area (m^2)
i, j	Particle number
L	Liquid
q	Spectral heat flux (W/ m^{2}Hz)
Q	Heat flux (W/ m^2)
r	Distance between particles
S	Solid

Greek Symbols

α	Solid-liquid interaction strength
ε	Lennard-Jones parameter (J)
σ	Lennard-Jones parameter (m)
τ	Correlation time (s)
ϕ	Potential energy (J)
ω	Angular frequency (1/s)

Subscripts

ij	Between particle i and j

INTRODUCTION

With the recent advances in nanotechnologies, the thermal resistance at the solid-liquid interface is becoming more important in controlling heat transport at the nanoscale [Cahill 2003 and 2014]. Further understanding and controlling of the mechanism behind this interfacial thermal resistance is critical for future applications of nanotechnologies.

Molecular dynamics simulations are beneficial when studying the mechanism behind the solid-liquid interfacial thermal resistance, because the heat flux across the solid-liquid interface can be directly calculated and be made available for detailed analysis [*e.g.*, Xue 2003, Ohara 2005]. Before now, the conventional studies showed that nanostructures on a solid surface change the solid-liquid interfacial thermal resistance [*e.g.*, Wang 2011, Shibahara 2011], and the more detailed investigation is required to elucidate the mechanism of the thermal-transport change. Recently, Fujiwara [2019] investigated effects of the adsorbed atoms on the thermal resistance and showed that the adsorbed atoms on a solid surface affect the thermal resistance and thermal transport mechanism at the single-atom scale.

To understand the thermal-transport mechanism, the spectral analysis is a common technique, and a number of studies have used the VDOS (Vibrational density of states). In 2016, a spectral analysis was proposed, where the heat flux passing through a solid-liquid interface is decomposed into frequency components, which uncovered the dependence of the spectrum on the solid-liquid interaction strength when the solid surface is flat and smooth [Sääskiahti 2016, Giri 2016]. However, there is much to be uncovered on the details of heat transfer when there are nanostructures on a solid surface, and insights from the viewpoint of spectral analysis are lacking.

Therefore, this study aimed to understand how atomic structures on the solid surface affect the heat transport mechanism at the solid-liquid interface from the standpoint of spectral analysis. We changed the configurations of the attached atoms on a solid surface: adsorbed or clustered atoms, and investigated effects of them on the thermal resistance and the heat transport mechanism, based on the spectral heat flux. The spectral analysis was conducted focusing on the heat flux across the solid-liquid interface using molecular dynamics simulations.

CALCULATION SYSTEM AND NUMERICAL DETAILS

Figure 1 shows the calculation system in this study. As shown in Fig. 1, the liquid molecules exist between the solid walls at the top and bottom in the system. The system size is $L_x \times L_y \times L_z$=3.9 ×3.9 ×8.7 nm^3. The configurations of the adsorbed atoms or clustered atoms are shown in Fig. 2. In Fig. 2, the white atoms show (a) adsorbed atoms or (b) clustered atoms. As the models of the solid atoms and liquid molecules, Pt and Ar were adopted, respectively. The periodic boundary conditions were imposed in the x and y directions. The 12-6 Lennard-Jones potential was used as the potential function between the Pt atoms and between Ar molecules. For the interactions between the Pt atoms and Ar molecules, equation (1) was used.

$$\phi_{ij}(r_{ij}) = 4\alpha\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} \qquad (1)$$

Here, the parameter α represents the solid-liquid interaction strength, and, r_{ij} is the distance between the ith and jth particles, respectively. The parameters of σ = 0.254 nm and ε = 109.2×10^{-21} J [Zhu 1994] were used between the Pt atoms, while σ = 0.3405 nm and ε = 1.67×10^{-21} J were used between the Ar molecules. Note that the Lorentz-Berthelot rule was used for the Pt-Ar interaction parameters. The leapfrog method was used for the numerical integration, and the time step interval was 1 fs. The cutoff distance of the potential function was 3σ.

The calculation procedure is as follows. The temperature of the liquid was controlled to 100 K for 0.1 ns using the velocity scaling method. The top and bottom layers of the solid were controlled to 110 and 90 K, respectively, using the Langevin method [Tully 1980]. Then, the temperature control of the liquid was removed, and calculations were carried out for 2 ns. The heat flux and the thermal resistance were calculated using data over 5 ns.

The heat flux from the liquid to the solid, $Q_{\mathrm{L}\rightarrow\mathrm{S}}$, is obtained using the following Eq. (2).

$$Q_{\mathrm{L}\rightarrow\mathrm{S}} = \frac{1}{A}\sum_{j\in\mathrm{L}}\sum_{i\in\mathrm{S}}\langle \boldsymbol{F}_{ij} \cdot \boldsymbol{v}_i \rangle \qquad (2)$$

In Eq. (2), L and S represent the liquid and solid phase, respectively, $\boldsymbol{F}_{ij}$ is the force from particle j that is acting on the particle i, $\boldsymbol{v}_i$ is the velocity of the particle i, A is the area of the solid-liquid interface, and $\langle\quad\rangle$ is the time average. The spectral decomposition of Q, $q(\omega)$, is given by Eq. (3).

$$q_{\mathrm{L}\rightarrow\mathrm{S}}(\omega) = \frac{2}{A}\mathrm{Re}\left[\sum_{j\in\mathrm{L}}\sum_{i\in\mathrm{S}}\int_{-\infty}^{\infty}\mathrm{d}\tau\, e^{i\omega\tau}\langle \boldsymbol{F}_{ij}(\tau)\cdot \boldsymbol{v}_i(0)\rangle\right] \qquad (3)$$

Here, ω is the angular frequency, and τ is the correlation time between forces acting on the solid atom i and its velocity.

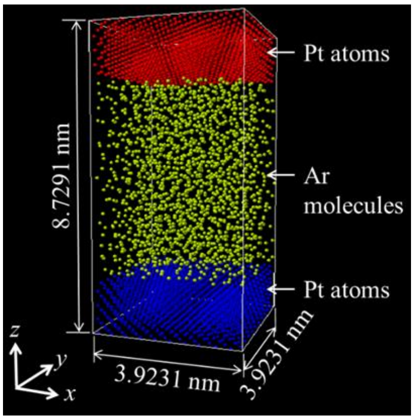
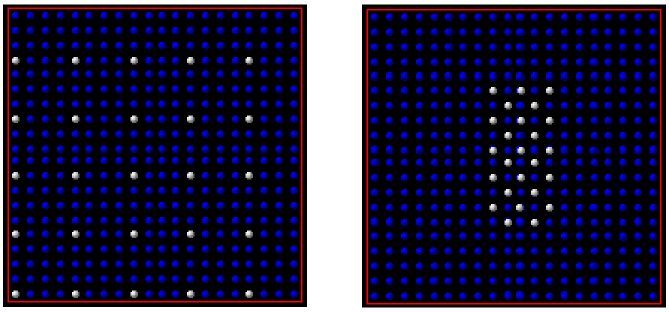


Fig. 1. Calculation model.

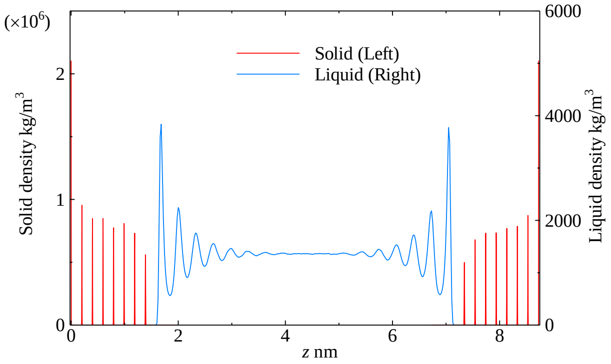


(a) Case 1. (b) Case 2.

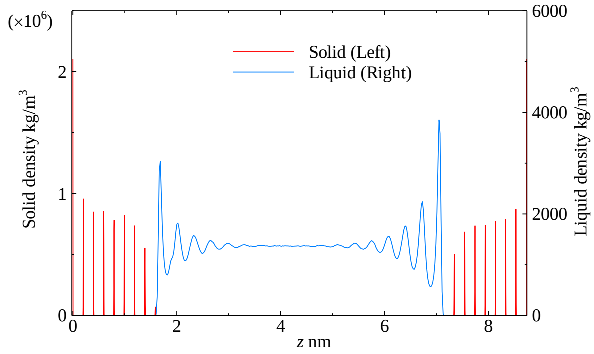
Fig. 2. Configuration of the attached atoms on a solid surface; (a) adsorbed atoms and (b) clustered atoms. The white atoms show the adsorbed atoms or clustered atoms on a solid surface.

RESULTS

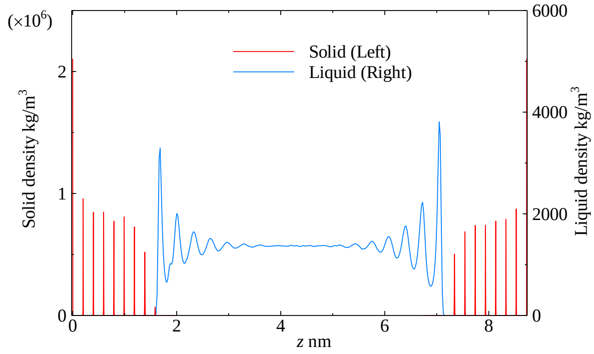
In Fig. 3, we present basic results of the calculation system in the case of α = 0.05: the density distributions of the solid and liquid phases; (a) Flat, (b) Case 1, and (c) Case 2. Here, the position of the lowest layer of the solid phase is chosen as z = 0.0, and it’s to be noted that the solid density doesn’t show the same value due to the high resolution in the *z* direction. Depending the structures on the solid surface, the liquid density distributions change in the vicinity of the lower solid surface, while the density distributions in the vicinity of the upper wall shows almost the same values. Especially, in Figs. 3(b) and 3(c), it's confirmed that not only the 1st layer of the liquid contacting the solid surface but also the 2nd layer are affected due to the attached atoms.



(a) Flat.



(b) Case1.



(c) Case2.

Fig. 3 Density distributions in the systems; (a) Flat, (b) Case1, and (c) Case2.

The results of the thermal resistances are shown in Fig. 4 for various values of α. The thermal resistances were calculated using the temperature jump and the heat flux across the interface [Fujiwara 2019]. As it is confirmed in Fig. 4, the thermal resistance of the flat solid surface is the highest compared with those of the surfaces with attached atoms: adsorbed or clustered atoms, which reveals that the attached atoms can enhance the thermal transport at the solid-liquid interface. Comparing the results of the surfaces with the adsorbed atoms (Case 1) and the clustered atoms (Case 2), it is found that the higher enhancement of the thermal transport can be observed for the surface with the adsorbed atoms than the clustered-atoms' case in the almost all cases of α.

Figure 5 shows the spectral heat flux $|q(\omega)|$ with its components in the case of the flat surface ($\alpha = 0.05$). The z and xy components shown in Fig. 5 represent the z and xy modes which are the components of the inner product of **F•v**: $F_z v_z$ and $F_x v_x + F_y v_y$, in Eq. (3). The result reveals that the intensity of the spectral heat flux (total) corresponds to the z mode, which indicates that the mode vertical to the interface is the main factor to transfer the thermal energy. For the z mode, the dominant frequency is 4 THz, while the xy mode has the peak value at 2.5 THz in the frequencies which was extremely weak in this study.

Furthermore, the spectral heat flux for the cases: flat, adsorbed atoms, and clustered atoms, are plotted in Fig. 6. Figure 6 shows that the low frequencies (2THz) are dominant for the thermal transport in the Case 1, where the adsorbed atoms exist on the solid surface. On the other hand, in the Case 2, such peak value at the low frequencies is not observed. The peak value at the 4 THz was not detected in the cases with attached atoms. That is, the spectral thermal transport mechanism depends on the structures on the solid surface, and especially for the cases of the adsorbed atoms, the thermal transport with the low frequencies enhance the thermal transport and reduce the thermal resistance.

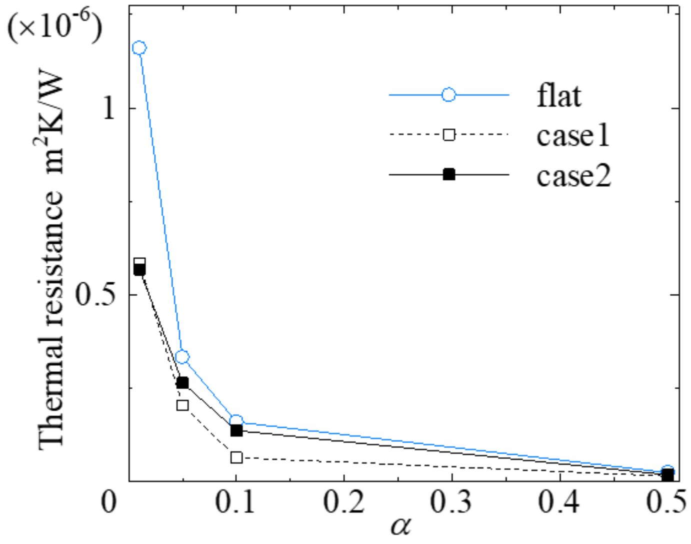


Fig. 4 Thermal resistance for various values of α (Flat, Case 1, and Case 2).

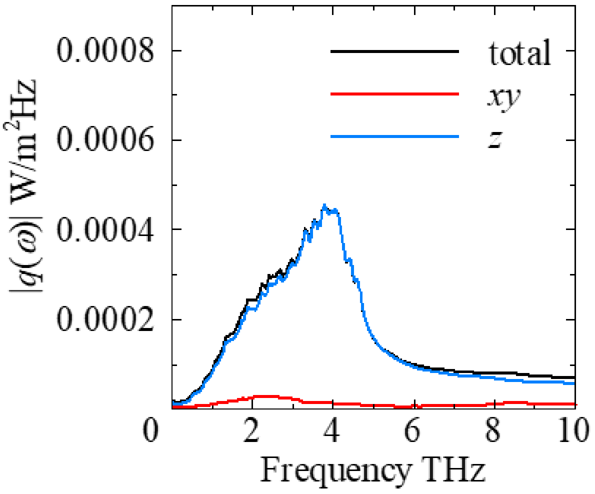


Fig. 5 Spectral heat flux with its components in the case of the flat surface.

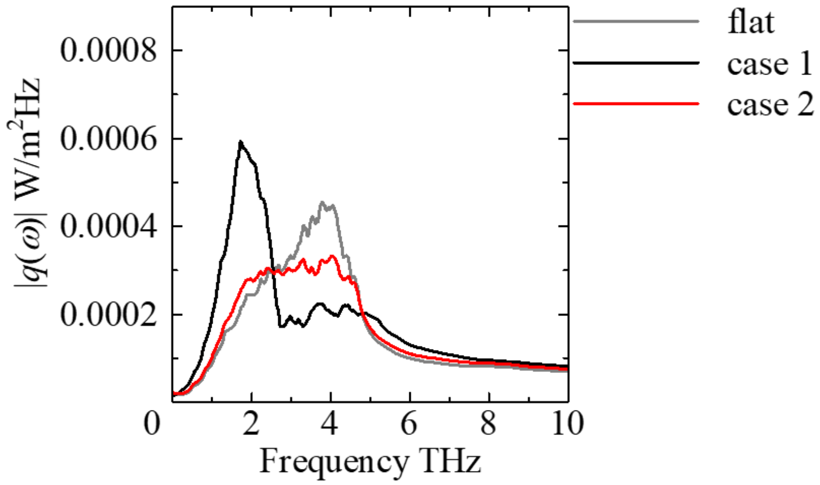


Fig. 6 Spectral heat flux for various cases.

CONCLUSION

This study examined effects of structures at the atomic scale on heat transfer mechanisms between a solid and liquid interface, using molecular dynamics simulations. We prepared the three cases of the surface: flat surface, surface with attached atoms (adsorbed and cluster atoms), and the effects of the structures and solid-liquid interaction strengths on the thermal resistance and spectral heat-transport mechanism were investigated. The results revealed the enhancement of the thermal transport is remarkable for the surfaces with attached atoms, and in particular the surface with the adsorbed atoms can reduce the thermal resistance. Compared with the results of the flat surface, the surfaces with the attached atoms didn't show the peak value at the high frequencies in the spectral heat flux. We found that the strong spectral thermal-transport was detected at the low frequencies in the case of the surface with the adsorbed atoms, which is related to the mechanism to enhance the thermal transport by the adsorbed atoms.

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