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# A molecular dynamics study on the effect of surfactant adsorption on heat transfer at a solid-liquid interface



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# ABSTRACT

Molecular dynamics simulations of a liquid layer between solid surfaces under a temperature gradient were performed to investigate the mechanism by which solid-liquid interfacial heat transfer is affected by adsorption of surfactant on solid surfaces with various concentrations of surfactant. The surfactant and solvent were chosen to be single-atom molecules with a contact angle of 0 and 180 degrees to the solid surface, respectively. Density distributions showed that the surfactant molecules formed a layer on the solid surface. The heat flux across the solid-liquid interface and between two adsorption layers closest to the surface was decomposed into energy transport terms based on molecular motions and inter-molecular interactions to examine the molecular mechanism of heat transfer. The interfacial thermal conductance (ITC) was also evaluated, and the molecular mechanism contributing to it was analyzed. It was found that the surfactant molecules that were adsorbed onto the solid surface decreased the interfacial thermal resistance, causing an increase in the heat flux, where the heat path from the solid to the solvent molecules via surfactant molecules became dominant as compared with the direct path from the solid to solvent molecules. It resulted in the temperature of surfactant being closer to the temperature of the solid than that of solvent in the vicinity of the solid surfaces. This indicated that in order to increase heat transfer via surfactants, not only the surfactant affinity with solid surface, but also the surfactantsolvent affinity must be considered. The contribution of each surfactant molecule to the ITC was greater than that of each solvent molecule, and both were proportional to their intermolecular potential with the solid atoms. Also, the contributions of a single surfactant and solvent molecule to the ITC were independent of their concentrations in the adsorption layer.

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### 1. Introduction

Interfacial thermal energy transfer at a solid-liquid interface is an important subject in the research field of heat transfer and has been widely investigated. Operating requirements of significant thermal energy transfer occur in the case of power modules where various components such as electrodes and insulating plates form multilayer structures. Recently the thermal resistance at the joint interfaces of these components has become a serious obstacle to efficient heat dissipation. Thermal interface materials (TIMs) [1,2], which are mostly liquids and soft matters, are usually applied to fill the gap at the joint interface. In such cases, to achieve high thermal transport, efficient reduction of the interfacial thermal resistance at the TIM-solid interface is indispensable. In the present paper, the adsorption of surfactant on solid-liquid interfaces and its thermal effects are examined in order to study the application of surfactant additives to liquid TIMs.

Surfactants are widely utilized in surface modification at the solid-liquid interface where they are applied to the liquid as additives to form an adsorption layer on the solid surfaces and provide protection for the solid surfaces through reduction of friction and so on. Although surfactants are inferior in the stability of their adsorption layers when compared to the chemical adsorption systems like self-assembled monolayers (SAM) [3–5], and hard coating [6–8] prepared by special production processes, the use of adsorbed surfactants has significant advantages; they are easy to use and self-repairing, i.e. even if the layer of surfactants covering the solid surface is broken, surfactant molecules return to their original states immediately due to re-adsorption and form a soft coating layer. This phenomenon is often described as dynamic coating to cover the solid surfaces and modify the surface characteristics.

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With respect to the application of surfactants to interfacial heat transfer, except for the studies of boiling heat transfer [9-11] where surfactants affect bubble formation via the reduction of liquid-vapor interfacial tension, only scant attention has been paid to their effect on interfacial heat transfer. Recently, a few studies have demonstrated the effectiveness of the application of surfactants on interfacial heat transfer. The interfacial thermal conductance (ITC) of a system with two surfactant types in an aqueous solution in contact with a gold nanorod was investigated via both experiments and molecular dynamics (MD) simulations [12].

However, to the best of the authors' knowledge, there has been no significant reports of research on the molecular mechanism of solid-liquid interfacial heat transfer that determine the characteristics of the ITC when the surfactants are adsorbed at a solid-liquid interface. Surfactants have great potential for controlling interfacial heat transfer due to their ease of use and high selectivity for surface adsorption. In order to improve the applicability of surfactants to interfacial heat conduction control, it is important to understand the molecular mechanism of interfacial heat transfer, not only to help providing reasonable views of complicated interfacial phenomena, but also to assist in finding the substances having desirable interfacial heat conduction properties.

The present study uses molecular dynamics simulation of heat conduction in a system for a liquid in contact with a solid surface. We added a surfactant to the liquid at various concentrations and examined the adsorption of surfactant to the solid-liquid interface as well as its effect on heat conduction properties. Adsorption is a complicated process that is affected by various factors including the roughness and geometry of the solid surface [13], the flexibility and molecular topology of the surfactant [14], and the strength of interfacial coupling between solvent and surfactant [15]. Considering the complexity of adsorption, the surfactant and the solvent were assumed to be monatomic molecules, in order to concentrate on the fundamental mechanism involved in the effect of adsorption on heat transfer. The analysis of density distributions and adsorption of surfactant at different surfactant concentrations is given in Section 3.1. The manner in which the temperature distribution, heat flux and ITC changed with the surfactant adsorption are discussed in Section 3.2, molecular mechanisms that determine the macroscopic heat flux and ITC are decomposed and analyzed in Section 3.3, where the relation between ITC and the interfacial potential energy is also demonstrated.

#### 2. Simulation details

In the present study, the heat conduction model was built as shown in Fig. 1. The model consists of two solid walls and a liquid between the two walls, in which a surfactant was dissolved into a solvent. Vacuum existed outside the walls in the z direction and there were no external interactions. The periodic boundary condition was applied for the x and y directions.

The liquids, i.e., the solvent and surfactant, were assumed to be simple liquids consisting of monatomic molecules. The interaction potential between liquid atoms (surfactant and solvent) was expressed by the Lennard-Jones (LJ) potential as:

$$\phi(\mathbf{r}_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma_{ij}}{\mathbf{r}_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{\mathbf{r}_{ij}} \right)^6 \right],\tag{1}$$

where  $r_{ij}$  is the distance between *i* and *j* atoms, and  $\varepsilon$  and  $\sigma$  are the energy and distance parameters, respectively. For liquid-liquid interactions (solvent-solvent, surfactant-surfactant and solvent-surfactant), the parameters for argon were used [16]:  $\sigma = 3.4236$  Å,  $\varepsilon = 1.65 \times 10^{-21}$  J, and mass of the surfactant and solvent was given as  $6.63 \times 10^{-26}$  kg.



**Fig. 1.** Diagram of the heat flow model, where the positions of the outermost layers of the solid (silver color) are fixed, the dark red layer is set as the heat source, the red layers are the solid on the high temperature side, the blue layers are the solid on the low temperature side, the dark blue layer is set as the heat sink, the orange spheres are the surfactant molecules and the green spheres are the solvent molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Each of the solid walls was a FCC crystal of platinum with its (1 1 1) surface contacting the liquid. The interaction between the solid atoms was modeled by the Morse potential:

$$\phi(r_{ij}) = D[e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)}], \qquad (2)$$

where  $D = 6.617 \times 10^{-20}$  J,  $r_0 = 2.7738$  Å,  $\alpha = 1.85$  Å<sup>-1</sup>, and mass of the solid atom was  $3.23 \times 10^{-25}$  kg [17].

The LJ potential was also used for the interaction between the solid atoms and the solvent or surfactant molecules, where  $\sigma$  = 2.935 Å was kept to be the same as the Ref. [18] for argon and platinum, and  $\varepsilon$  was set according to Table 1. The  $\varepsilon$  values were chosen so that the contact angle of the surfactant and solvent with the solid FCC (1 1 1) surface would be 0 (complete wetting) and 180 (complete drying) degrees, respectively. The work of Spijker [18] was used to determine the values of  $\varepsilon$  according to the above contact angles. The present temperature setting was slightly different from the reference, but the influence of temperature on the contact angle is negligible [19]. A potential cutoff radius of 3.5 $\sigma$  was used for all interactions and a time step of 1 fs was used for all simulations.

Here, the construction of the system is described in detail. Each solid wall consists of seven layers with 224 atoms per layer. The thickness of each layer is 0.226 nm. The dimensions of the simulation system are 3.74 nm and 3.76 nm in the *x* and *y* directions, respectively. The distance in the *z* direction between outermost molecular layers of the two walls is in the range between 9.117 nm and 9.564 nm, which was determined for each simulation case according to the pressure control scheme described later. Liquid consists of 1600 atoms including solvent and surfactant molecules. The simulation parameter is the concentration conditions are shown in Table 2.

Next we describe the scheme that was used to obtain the distance in the *z* direction between the outermost molecular layers that is shown in Table 2. Initially, the outermost molecular layer of the left solid wall was positioned at z = 0, and the outermost

 Table 1

 Interaction parameters between different molecule types.

| $\epsilon \; [\times 10^{-21} \; J]$ |
|--------------------------------------|
| 1.65                                 |
| 1.25                                 |
| 0.33                                 |
|                                      |

| Number of surfactant and solvent molecules in systems, dimension of the simulation system in the <i>z</i> direction, and density of the liquid with different concentration conditions. |        |   |                       |                    |  |  |  |
|---|--------|---|-----------------------|--------------------|--|--|--|
|   | System | Concentration of surfactant, $c_{surf}$ | Number of surfactants | Number of solvents | Dimension in the <i>z</i> direction [nm] | Density of the liquid [kg/m <sup>3</sup> ] |  |
|   | 1      | 0%                                      | 0                     | 1600               | 9.564                                    | 1143.86                                    |  |
|   | 2      | 1%                                      | 16                    | 1584               | 9.564                                    | 1135.40                                    |  |
|   | 3      | 2%                                      | 32                    | 1568               | 9.532                                    | 1130.21                                    |  |
|   | 4      | 3%                                      | 48                    | 1552               | 9.398                                    | 1151.92                                    |  |
|   | 5      | 4%                                      | 64                    | 1536               | 9.398                                    | 1144.90                                    |  |
|   | 6      | 5%                                      | 80                    | 1520               | 9.380                                    | 1140.64                                    |  |
|   | 7      | 6%                                      | 96                    | 1504               | 9 326                                    | 1158 98                                    |  |

1472

1440

1360

1280

800

0

molecular layer of the right solid wall was positioned at z = 9.564 nm. The surfactant molecules were placed randomly in the vicinity of the solid surfaces, distant from the solid surface by more than 0.3 nm and less than 1 nm, and solvent molecules were randomly placed between the surfactant regions mentioned above. An equilibrium molecular dynamics (EMD) simulation was performed at the temperature of 120 K with a Nosé-Hoover thermostat for a run of 10 ns. After the system was equilibrated, a non-equilibrium molecular dynamics (NEMD) simulation was then conducted with the pressure set at 4.5 MPa by the fluctuating walls method [20], by imposing a constant external potential; two virtual walls were placed outside both the solid walls, and the internal pressure was controlled by applying a constant force to these virtual walls directed inwards to the system. The interaction potential between the virtual walls and the solid walls was expressed as follows:

128

160

240

320

800

1600

Table 2

8

9

10

11 12

13

8%

10%

15%

20%

50%

100%

$$E(Z) = \frac{\pi\rho D}{2\alpha^2} \left\{ \left( Z + \frac{1}{2\alpha} \right) e^{-2\alpha(Z-r_0)} - 4 \left( Z + \frac{2}{\alpha} \right) e^{-\alpha(Z-r_0)} \right\},\tag{3}$$

where Z is the distance between the solid atoms and virtual wall. The parameters were set as  $\rho D = 3.7 \times 10^9 \text{ J/m}^3$ ,  $r_0 = 2.885 \text{ Å}$  and  $\alpha$  = 1.3393 Å<sup>-1</sup>. The mass of the virtual wall is 8.335 × 10<sup>-25</sup> kg. The second outermost outer layers of the left and right solid walls were kept at a constant temperature of 146 K and 93 K, respectively, via velocity scaling. In the meanwhile, the solid walls with the liquid in between were set to be movable freely for 10 ns, and the dimension of the system in the z direction was obtained from a subsequent run of 5 ns, as shown in Table 2. The target pressure mentioned above was set to the value of the critical pressure of the liquid with the critical temperature of approximately 146 K, in order to avoid vaporization on the high temperature side of the system. This resulted in a slightly compressed liquid, where the average density of the liquid between the two solid walls was in the range of 1.10 g/cm<sup>3</sup> to 1.17 g/cm<sup>3</sup>, and the density of liquid in the bulk region at the middle of the system away from the solid walls (see Fig. 2) is shown in Table 2. The value of the critical pressure was obtained from the study of Dunikov et al. [21].

Here we describe the construction of systems used for nonequilibrium molecular dynamics (NEMD) to examine the mechanism of energy transfer associated with the adsorption at the solid-liquid interface. The outermost laver of the left solid wall was fixed at z = 0, and the outermost layer of the right solid wall was fixed at the position shown in Table 2 as the dimension in the z direction. The volume of the simulation system was kept constant. The second outermost outer layers of the left and right solid walls were kept at different temperatures as in the previous paragraph, which generated a heat flux across the liquids along the z direction. Although the pressure of the system changes slightly due to fixing the walls, the change is smaller than 1.9 MPa in all the simulation cases and its influence on heat transfer is negligible. The analysis data was obtained for a run of 15 ns after 10 ns of equilibration run with heat flux at which time the system had reached a steady state.

1161.09

1158.45

1137.95

1141.95

1125.70

1146.31

## 3. Results and discussion

9.310

9.283

9.271

9 2 0 7

9.187

9.117

## 3.1. Adsorption of surfactant at the solid-liquid interface

Examples of the density distributions of surfactant, solvent and solid are shown in Fig. 2 for the cases of  $c_{surf} = 0\%$  and 5%. The profiles were obtained by dividing the system into 10,000 slabs along the z-axis with a slab width of approximately 0.01 Å. The left panel of Fig. 2 shows the case without surfactant. The densities exhibit higher values on the right side as compared with the left side because of the lower temperature on the right side. The right panel shows the case of  $c_{surf}$  = 5%. Adsorption of surfactant molecules onto the solid surface is clearly observed. The top of the density peak of the adsorption layer is almost comparable to that of the solvent, although the average concentration,  $c_{surf}$  is only 5%.

The degree of surfactant adsorption onto the solid-liquid interface was quantified as the area number density of the surfactant molecules in the adsorption layer,  $N_{surf}^{ads}$ , which was obtained by integrating the density of the surfactant along the z-axis from the excluded volume area at the solid-liquid interface to the minimum liquid density between the first and second adsorption lavers, i.e. integrating over the first adsorption layer as seen in Fig. 2. The  $N_{\rm surf}^{\rm ads}$  as a function of the surfactant concentration,  $c_{\rm surf}$  is shown in Fig. 3 for both high and low temperature sides. Even at the same concentration, the  $N_{\rm surf}^{\rm ads}$  on the high temperature side is lower than that on the low temperature side. It is found that as  $c_{surf}$ increases, rapid growth of the adsorption layer of the surfactant appears in the range of low  $c_{surf}$ . At  $c_{surf} = 10\%$ ,  $N_{surf}^{ads}$  is almost half of  $N_{surf}^{ads}$  at  $c_{surf} = 100\%$ , and the growth becomes slower as the amount of surfactant adsorption on the solid surface approaches saturation.

### 3.2. Temperature distribution and heat flux

Fig. 4 shows the temperature distributions of the solid, solvent and surfactant for the cases of  $c_{surf}$  = 0% and 5%. The temperature of surfactant molecules in the bulk region is not shown because of the high uncertainty due to the low number of molecules.

There are significant temperature jumps at the solid-liquid interfaces in Fig. 4 due to the existence of thermal boundary resistance. An interfacial phenomenon is observed in the right panel of



Fig. 2. Density profiles of surfactant, solvent and solid for the cases of  $c_{surf} = 0\%$  (left) and 5% (right), where the fixed layers and heat source/sink layers of the solid wall are not shown.



**Fig. 3.** Area number density of surfactant molecules adsorbed on the solid surface,  $N_{\text{surf}}^{\text{ads}}$ , at different surfactant concentrations.

Fig. 4, where a temperature difference appears between the solvent and surfactant in the vicinity of the solid surface, the temperature of the surfactant is about 2 K closer to the solid temperature than that of the solvent. This implies that more thermal energy is transferred between the solid surface and the surfactant molecules than between the solid surface and the solvent molecules, and a heat path exists from the solid surface to the solvent molecules via the surfactant molecules. This point will be examined later in the following Section 3.3.

The heat flux across a control surface and the heat flux averaged by integration along the length of the control volume are expressed by [22]:

$$J_{z}S_{xy} = \sum_{i}^{\Delta t = 1fs} \left[ \left[ \left( \frac{1}{2}mv_{i}^{2} + \phi_{i} \right) \middle/ \Delta t \right] \frac{v_{i,z}}{|v_{i,z}|} + \frac{1}{2} \sum_{i} \sum_{j>i} \left[ F_{ij} \cdot (v_{i} + v_{j}) \frac{z_{ij}}{|z_{ij}|} \right] \right], \quad (4)$$

$$J_z V = \sum_i \left(\frac{1}{2}m\nu_i^2 + \phi_i\right) + \frac{1}{2}\sum_i \sum_{j>i} \left[F_{ij} \cdot (\nu_i + \nu_j)z_{ij}^*\right].$$
 (5)

Here  $J_z$  represents the heat flux along the *z*-axis, *m* and *v* denote the mass and velocity of molecules, while  $z_{ij}$  and  $F_{ij}$  denote the distance and force between molecules, respectively. Eq. (4) represents the amount of heat flux across a control surface, and Eq. (5) is obtained by integrating the first equation along the length of the control volume in the direction of the heat flux to obtain an averaged heat flux. The first term of both equations represents the kinetic and potential energy carried by the molecules passing through the control surface or inside the control volume, while the second term stands for the heat transfer associated with the interaction between molecules.

Based on Eqs. (4) and (5), heat flux at several control surfaces and a control volume were observed to examine the molecular mechanism of thermal energy transfer. According to the density distributions of the surfactant and solvent, four control surfaces and a single control volume were placed in the system as shown in Fig. 5. The control surfaces denoted by "Interface 1" and "Interface 2" are the interfaces between liquid and solid surfaces on the high temperature and low temperature sides, respectively, with no molecules crossing these control surfaces. The control surfaces "Interlayer 1" and "Interlayer 2" are at the minimum of the liquid density profile between the first and second adsorption layers of the solvent on the high temperature and low temperature sides, respectively. These control surfaces work to discriminate the surfactant molecules in the adsorption layer on the solid surface from the bulk liquid molecules. The control volume in the bulk liquid for Eq. (5) was set at 3.5 < *z* < 5.5 nm.

Fig. 6 shows the heat flux in the control volume as a function of the surfactant concentration,  $c_{surf}$ . Because the temperature difference between the heat source (the high temperature solid wall) and the heat sink (the low temperature solid wall) is fixed in the





**Fig. 5.** Positions of the control surfaces (Interface 1, Interlayer 1, Interface 2, Interlayer 2) and control volume (Bulk), used to examine heat flux.

present simulation, the heat flux is determined by the overall thermal resistance between the heat source and the heat sink. As we can see in Fig. 4, the major contributor to the overall thermal resistance between the solid walls is the solid-liquid interfacial thermal resistance. As  $c_{surf}$  increases and the amount of the adsorption layer of the surfactant grows rapidly in the range of low  $c_{surf}$ , the solidliquid interfacial thermal resistance decreases, which results in the rapid increase of the heat flux observed in Fig. 6.

The temperature jump  $\Delta T$  at the solid-liquid interface was obtained by an extrapolation method as follows. A linear approximation was applied to each of the temperature distributions in the liquid and solid, as shown in Fig. 4. Here the data for the fixed layer, heat source/sink layer, and surface layer of the solid atoms and the first and second adsorption layer of liquid molecules were eliminated from the approximation. Two straight lines were extrapolated to the position of the solid-liquid interface, which was determined as the center position between the peak position of the surface layer of solid atoms and the peak position of the adsorbed layer of liquid molecules in the density distribution profile. The temperature jump was obtained as the difference between the two extrapolated temperatures at the solid-liquid interface. A trend was found that the temperature jump decreases as  $N_{\rm surf}^{\rm ads}$ increases, varying from 23.67 K to 14.53 K in the range of 0% to 100% for  $c_{\text{surf}}$ .

The interfacial thermal conductance (ITC) is evaluated by

$$G = \frac{-J_z}{\Delta T},\tag{6}$$

where  $J_z$  is the heat flux in the direction of z, and  $\Delta T$  is the temperature jump at the solid-liquid interface described above.



**Fig. 6.** Heat flux in the bulk liquid region with different concentrations of surfactant. The standard error of the mean is shown as an error bar.



**Fig. 7.** ITC as a function of concentration of surfactant, *c*<sub>surf</sub>, at the high temperature and the low temperature interfaces.

Fig. 7 shows the ITC as a function of the surfactant concentration at high temperature and low temperature interfaces. There is a slight difference in ITC between the high and low temperature sides. This is mainly due to two factors. The first one is the density of the liquid in the adsorption layer. The liquid density in the vicinity of the solid surfaces is higher on the low temperature side, which means that more molecules take part in the interfacial heat transfer and results in a higher ITC. A similar phenomenon has been observed for the interface between a solid and a pure liquid [23]. Another factor is the adsorption of surfactant. As was observed in Fig. 3, a higher amount of the surfactant molecules is adsorbed onto the interface on the low temperature side, which increases the ITC. The response of ITC to  $c_{surf}$ , especially the rapid increase in the range of low  $c_{surf}$ , is similar to that of the heat flux shown in Fig. 6. This is particularly important when considering real applications, as by only adding 6% surfactant to the solvent, the ITC has almost tripled, which demonstrates that surfactants can have a significant effect on improving interfacial heat conductance.

## 3.3. Intermolecular energy transfer over the interface

The heat flux is broken down into seven terms depending on the energy transfer mechanisms, which consists of the transport of potential energy and kinetic energy due to molecular motion,



**Fig. 8.** Contributions of each molecular mechanism of thermal energy transfer to the macroscopic heat flux observed at the interfaces, interlayers and the bulk liquid region, which consist of potential energy transport, kinetic energy transport, and virial terms composed of IETs between surfactant-surfactant, solvent-solvent, surfactant-solvent, surfactant-solvent, surfactant-solvent, surfactant-solvent, is 6%.



**Fig. 9.** Contributions of each molecular mechanism of thermal energy transfer to the macroscopic heat flux as functions of the area number density of the surfactant molecules in the adsorption layer,  $N_{surf}^{ads}$  ((a), (b), (d), (e)) or the concentration of surfactant in the liquid,  $c_{surf}$  ((c)). Only the cases for  $0 \le c_{surf} \le 20\%$  are plotted. (a) at the solid-liquid Interface 1, (b) at the Interlayer 1 between the two adsorption layers close to the solid surface, (c) at the bulk liquid far from the solid surface, (d) at the solid-liquid Interface 2, (e) at the Interlayer 2. See Fig. 5 for their locations. The standard error of the mean of the total heat flux is shown as an error bar.



**Fig. 10.** Contributions of the surfactant-solid and solvent-solid IETs to the interfacial thermal conductance (ITC) as functions of the area number density of the surfactant molecules in the adsorption layer,  $N_{surf}^{ads}$ . Only the cases for  $0 \le c_{surf} \le 20\%$  are plotted.

and the virial terms composed of intermolecular energy transfer (IET) between surfactant-surfactant, solvent-solvent, surfactant-solvent, surfactant-solid and solvent-solid. A similar analysis has been reported by the authors for a bulk mixture of simple liquids [24].

The contributions to the total heat flux at the four control surfaces and one control volume as shown in Fig. 5 were obtained, and the result for the case of  $c_{surf} = 6\%$  is shown in Fig. 8 as an example. The standard error of the mean in the total heat flux was in the range of 1.06% to 9.95%. The composition of the heat flux varied depending on the location, while the total was almost constant within the standard error of the mean. Similar composition distributions were observed for both the high and low temperature sides. When compared with the transport of potential and kinetic energy carried by molecular motion, the virial terms, caused by IETs, dominate the heat flux in the systems, which is consistent with the past studies [22,25].

The heat flux across the solid-liquid interfaces (Interface 1 and 2) consists entirely of the surfactant-solid and solvent-solid IETs, since there are no liquid molecules crossing over the interfaces. At the interlayers, most of the contribution comes from the surfactant-solvent IET. On the other hand, the solvent-solvent contribution dominates in the bulk liquid region because there are few surfactant molecules.

The contributions of each molecular mechanism of thermal energy transfer to the macroscopic heat flux are shown in Fig. 9 for the cases of  $c_{surf}$  ranging from zero to 20%. The heat fluxes across the control surfaces are shown as functions of the area number density of surfactant in the adsorption layer,  $N_{surf}^{ads}$ , while the heat flux in the control volume of bulk liquid region is shown as a function of concentration of surfactant,  $c_{surf}$ . The relation between  $N_{\text{surf}}^{\text{ads}}$  and  $c_{\text{surf}}$  is shown in Fig. 3. The contributions of each molecular mechanism to the heat flux across the interfaces are shown in Fig. 9(a) and (d). When  $N_{surf}^{ads}$  is zero, the heat flux is contributed only by the solvent-solid IET. When  $N_{\text{surf}}^{\text{ads}}$  increases, the solvent-solid IET only decreases slightly due to the decrease of solvent concentration at the interface. The contribution of the surfactant-solid IET increases rapidly with the increase of  $N_{\text{surf}}^{\text{ads}}$ which results in the increase of the total heat flux. The surfactant-solid IET is comparable to the solvent-solid IET at  $0.7 < N_{surf}^{ads} < 0.8 \text{ nm}^{-2}$ , and becomes a dominant factor at larger  $N_{\rm surf.}^{\rm ads}$  This is a direct indication that the surfactant molecules adsorbed on the solid surface transfer more energy from the solid to enhance thermal energy transfer over the solid-liquid interface.

Fig. 9(b) and (e) show the contributions of each molecular mechanism to the total heat flux across the interlayers between the first and second adsorption layers of the liquid molecules near the surfaces, which is mainly composed of the IETs of surfactantsolvent, solvent-solvent and surfactant-surfactant, and the kinetic and potential energy transport due to molecular motion. The contributions of the surfactant-solid and solvent-solid IETs are negligible, because of the distance of the liquid molecules from the solid surface. The contributions of transport of potential and kinetic energy due to molecular motion show no obvious correlation to  $N_{\rm surf}^{\rm ads}$ , suffering from their non-negligible fluctuation. The contribution of the surfactant-solvent IET shows a remarkable increase as  $N_{\rm surf}^{\rm ads}$  increases, which suggests that the surfactant molecules in the adsorption layer further transfer thermal energy to the bulk solvent. In summary, as the adsorbed layer of surfactant molecules grows, the solid-surfactant IET increases at the solid-liquid interface and the surfactant-solvent IET increases at the interlaver between the two adsorption layers closest to the solid surface. This finding suggests that there is a dominant heat path from the solid to the bulk liquid via the surfactant molecules. The surfactant molecules in the adsorption layer indirectly enhance interfacial heat transfer between solid and solvent molecules, therefore their affinity with both solid and solvent molecules is important. These characteristics of molecular thermal energy transfer in the solid-liquid interface region are significantly different from those in the bulk liquid region, which is shown in Fig. 9(c).

The interfacial thermal conductance (ITC) can also be decomposed into contributions of molecular mechanisms of thermal energy transfer, which is referred here as the partial ITC. The surfactant-solid partial ITC and the solvent-solid equivalent obtained at the solid-liquid interfaces are plotted in Fig. 10 as functions of  $N_{\text{surf}}^{\text{ads}}$ . The increase in ITC at the interfaces according to the increase in  $N_{\text{surf}}^{\text{ads}}$  is more rapid than that of the heat flux shown in Fig. 9(a) and (b) because the temperature jump at the interfaces is smaller at higher  $N_{\text{surf}}^{\text{ads}}$ . The total ITC at  $N_{\text{surf}}^{\text{ads}} = 3 \text{ nm}^{-2}$  is five times higher than that at  $N_{\text{surf}}^{\text{ads}} = 0$ .

To gain further insight into the thermal energy transfer of individual molecules, per-molecule contributions of the surfactant and solvent to ITC were evaluated by dividing the partial ITC due to the surfactant-solid or solvent-solid IETs shown in Fig. 10 by the area number density of surfactant molecules, or solvent molecules, respectively. They are plotted in Fig. 11 as functions of  $N_{surf}^{ads}$ . It is observed that the ITC due to each surfactant molecule does not change significantly with  $N_{\text{surf}}^{\text{ads}}$  and is independent of temperature, as is also the case for the ITC per solvent molecule. This tendency continues at higher  $N_{\text{surf.}}^{\text{ads}}$ . The change of total ITC does not affect the ITC of the single molecule contribution either. It is worthy to note that the ITC contributed by each surfactant molecule is approximately four times as high as that by each solvent molecule. This matches the fact that the intermolecular potential for the surfactant-solid interaction is set to be four times higher than that for the solvent-solid interaction, as described in Section 2. The correlation between the ITC and the solid-liquid affinity has often been discussed [26–28]. To examine it in the present system, the potential energy between the solid and the surfactant and that between the solid and the solvent were obtained by summing up the intermolecular potential across the interfaces and its correlation with their partial ITC is plotted in Fig. 12. The potential energy between the surfactant and the solid is distributed over a wide range according to the number of surfactant molecules adsorbed onto the solid surface and they have a linear correlation with its partial ITC over this range. The correlation between the partial ITC of solvent-solid and the potential energy lies on the same line as that of surfactant-solid, although the potential energy value range is much narrower. It is found that a general relationship



**Fig. 11.** Contributions to ITC by each surfactant and solvent molecule at the high temperature and the low temperature interfaces where the concentration of surfactant is  $0 \le c_{surf} \le 20\%$ .



**Fig. 12.** The partial ITC as a function of the interfacial potential energy of solid-surfactant and solid-solvent, (a) at the high temperature interface, (b) at the low temperature interface, for the concentration of surfactant at  $0 \le c_{surf} \le 100\%$ .

between ITC and solid-liquid affinity, that has been previously observed for many kinds of single-component liquid [26–28], still holds for the solid-liquid interface with surfactant additives. In other words, when the second liquid component – surfactant – is added to solvent, for the interactions between both the solid and surfactant and between solid and solvent, the linear dependence of their partial ITC on their solid-liquid affinity exists unaffected by the composition of the binary liquid mixtures or the adsorption behavior of surfactant.

#### 4. Conclusions

In the present study, we focused on the molecular-scale characteristics of heat transfer at a solid-liquid interface where a surfactant adsorbs onto the solid surface, in order to examine the effect of the surfactant additives on liquid TIMs applied between solid surfaces to improve heat conduction. MD simulations were performed with various concentrations of surfactants, where monatomic molecules were used for to represent molecular liquids.

It was demonstrated that the surfactant molecules adsorbed onto the solid surface play a prominent role in enhancing interfacial heat conduction. The analysis of density and temperature distributions revealed the dynamic transfer process of thermal energy at the interfaces where the thermal energy in the solid wall is transferred mainly to the surfactant molecules, and the surfactant molecules further transfer the energy to the solvent molecules. This process increases the total heat transfer across the solidliquid interface.

The total heat flux and its components corresponding to the mechanisms of thermal energy transfer across the solid-liquid interfaces and between adsorption layers (interlayers) were analyzed. As a result, with an increase of the surfactant molecules adsorbed at the interface, the IET between surfactant and solid molecules becomes the dominant contribution to the total heat flux across the solid-liquid interfaces, exceeding the IET between solvent and solid molecules. Meanwhile the IET between surfactant and solvent also gradually increases to become a major contributor to the total heat flux across the interlayers. Surfactantsolid affinity and surfactant-solvent affinity both play a significant role in the interfacial heat transfer. By evaluating the ITC and the contribution of the surfactant and solvent to it, referred to as the partial ITC here, it was found that the contribution of the surfactant and solvent to the ITC per molecule remains at an almost constant value when there is an increase in the number of these molecules in the adsorption layer. Thus, the partial ITC increases as the number of the molecules increases. The ratio of the per-molecule ITC of the surfactant to that of the solvent was approximately equal to

the ratio of the intermolecular potentials for surfactant-solid and solvent-solid molecules. Concerning the correlation between ITC and the solid-liquid affinity, there is a single linear correlation between the partial ITC of the solvent or surfactant and their potential energy at the interface.

The present study revealed the effect of a surfactant additive to solvents that enhances the solid-liquid ITC, where the molecular mechanism was examined via a system consisting of a single monatomic solvent and surfactant molecules. These effects and the mechanism will be examined further for the case of complex surfactants and solvents that are utilized in industrial applications in future work.

# **Conflict of interest**

The authors declared that there is no conflict of interest.

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