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Molecular dynamics study on the role of hydrogen bonds and interfacial heat transfer between diverse silica surfaces and organic liquids



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ABSTRACT

The understanding of interfacial heat transfer mechanism is increasingly significant since interfacial thermal resistance plays an important role in thermal management as the size of electronic devices decreases. In this work, interfacial heat transfer between five diverse silica surfaces and two organic liquids was studied using the molecular dynamics method. The two organic liquids are triacontane and triacontanol, which are either hydrogen bond incapable or capable, respectively. Silica surfaces with silanols show better thermal transport ability with triacontane/triacontanol because of a vibration matching effect. Increase of silanol area number density enhances the interfacial heat transfer for silica-triacontanol systems but has little effect for silica-triacontane systems because triacontane is hydrogen bond incapable. However, even for silica-triacontanol, the improvement of interfacial heat transfer does not scale proportionally to silanol area number density, since silanol-triacontanol and silanol-silanol hydrogen bonds are competing. The effective hydroxyl density is proved to reasonably explain this effect. Furthermore, temperature affects the interfacial heat transfer of silica-triacontanol systems vitally because both the number and lifetime of hydrogen bonds are reduced at higher temperature. The vertical orientation of triacontanol adsorbed onto the interface brings efficient heat paths via hydrogen bonds and alkyl backbones, which causes the interfacial molecular layers of triacontanol to have higher thermal conductivity in the direction normal to the interface.

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1. Introduction

The progress of modern technology is inseparable from the development of various electronic devices . With the increasing minimization and integration of electronic devices, their performance is continuously enhanced, accompanied by higher and higher power density [1]. Consequently, this raises the requirement of a sophisticated thermal management to ensure the suitable working temperature of electronic devices since their poor heat dissipation causes the build-up of heat and results in the performance degradation and malfunction of electronic devices. Previous work pointed out that 1 K can result in over 5 percent decrease in reliability of electronic devices is of particular importance.

Inside an electronic device, electronic components are joined and the local asperities on their surfaces limit their true contact

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As the scale of electronic devices decreases, the experimental investigation on their thermal management becomes more limited by both technical and cost issues, and the theoretical guidance provided by simulation methods becomes more important.

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Molecular dynamics (MD) simulation, which can provide the insight into the underlying physics of atomic level phenomena, has been proved to be an effective tool to uncover the heat transfer mechanism of solid-liquid interface [5–10]. Ye et al. conducted MD simulation to study the interfacial heat transfer of Al₂O₃-MXenesilicone rubber (SR) composite and pointed out that MXene sheets play the role of a phonon bridge between Al₂O₃ and SR to improve the heat transport performance of Al₂O₃-based TIMs [11]. Using the MD method, Zhang et al. demonstrated that the thermal conductance across the interfaces between graphene and poly(methyl methacrylate) (PMMA) can be improved by 273% if graphene is hydroxyl-functionalized [12], while the MD simulation of Wang et al. showed hydroxyl functionalization has little improvement in heat transfer between graphene and paraffin $(C_{30}H_{62})$ [13]. These works with seemingly contradictory results revealed that whether liquid is hydrogen bond (H-bond) capable or incapable, as well as whether there are hydrogen bonds at the interface, affects the interfacial heat transfer. Due to the high dielectric constant and selectivity for chemical modification, silica is widely used as a predominant dielectric within integrated circuits and as substrate in the design of nanoelectronic devices [14]. In addition, organic liquids, such as paraffin [13,15], are commonly applied as TIMs or matrices of composite TIMs. Thus, understanding the interfacial heat transfer mechanism between silica and organic liquids is of practical significance for the thermal management design in electronic packaging. Indeed, a series of MD works have been conducted to investigate the heat transfer of silica surfaces [16,17]. Utilizing the MD method to study the interfacial heat transfer between water and silica with hydrophilic (Si-OH) surface, Schoen et al. revealed that interfacial thermal resistance increased with the increase of temperature at the interface because high temperature is not conducive to the formation of hydrogen bonds [18]. Xu et al. performed MD simulations to compare the interfacial heat transfer of silica-water and gold-water interfaces, and the result showed that silanols can bridge the vibrational mismatch between the silica and water and form hydrogen bonds (H-bonds) with water, which leads to larger interfacial thermal conductance of the silica-water interface [19]. However, in the existing MD studies of solid-liquid interfacial heat transfer, where silica acted as the solid, inorganic small liquid molecules, such as water, are common for the liquid, and organic liquids, especially long-chain large molecules, are rare. Meanwhile, investigating the effect of diverse silica surface environments on the interfacial heat transfer is expected to bring new insight and be of great utility to future work.

In this work, molecular dynamics simulation was conducted to investigate the role of hydrogen bonds in interfacial heat transfer between diverse silica surfaces and organic liquids. Five silica surfaces hydroxylated with different area number density of silanol groups are selected, and triacontane (C₃₀H₆₂) and triacontanol (C30H62O) act as different organic liquids, which are respectively hydrogen bond incapable and capable. First, temperature and density distributions are studied, and interfacial thermal resistance is evaluated to characterize their interfacial heat transfer performances. Then, mechanisms of interfacial heat transfer are uncovered by analyzing interfacial potential energy, vibrational density of states (DOS), and orientation of liquid molecules. We show that interfacial vibration matching determines the heat transfer at the silica-triacontane interface, whereas the formation of hydrogen bonds plays crucial roles at the silicatriacontanol interface. Lastly, the effective hydroxyl density proposed by Xu et al. [19], in addition to the effect of temperature, is proved to successfully estimate the interfacial heat transfer of silica-triacontanol systems.



Table 1	
Hydroxyl density of diverse silica surfaces.	

Silica type	Hydroxyl density
SiO ₂ (OH) ₀	0 nm ⁻²
SiO ₂ (OH) _{0/1}	2.4 nm ⁻²
SiO ₂ (OH) ₁	4.7 nm ⁻²
SiO ₂ (OH) _{1/2}	6.9 nm ⁻²
SiO ₂ (OH) ₂	9.4 nm ⁻²

2. Simulation methods

2.1. Simulation system

Fig. 1 depicts the schematic of simulation model in this work, where two silica walls sandwiched organic liquids along the *z* direction. Five silica surfaces of α -cristobalite or α -quartz, hydroxylated with different area number density of silanols on the surface, were selected (Fig. 2), taken from the work of Emami et al. [20]. For convenience, they were named as SiO₂(OH)₀, SiO₂(OH)_{0/1}, SiO₂(OH)_{1/2}, and SiO₂(OH)₂, respectively, where the subscript *n* of SiO₂(OH)_n indicates the number of silanol groups linking to a single superficial silicon atom. Thus, the hydroxyl area density of each silica surface is in the range of 0 to 9.4 per nm² (Table 1). These five silica models can characterize silica with different crystal cleavage planes, crystal sizes, porosity, pH, and thermal pretreatments. More details of these silica walls are provided in Section S1 of Supporting Information.

With the aim of studying roles of hydroxyl groups, as well as effects of liquid structure, in the interfacial heat transfer, two organic liquids were chosen. One is triacontane ($C_{30}H_{62}$), a long chain linear alkane that cannot form hydrogen bonds, and the other is triacontanol ($C_{30}H_{62}O$), a long chain linear alcohol that can form hydrogen bonds. For both liquid types, the number of liquid molecules in the simulation system was 800.

All simulations in the present work were implemented using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [21], and atoms were visualized using Visual Molecular Dynamics (VMD) software [22]. The following potential energy expressions were adapted to describe atomic interactions of diverse silica [20]:

$$E_{pot} = \sum_{ij,nonbonded} \varepsilon_{ij} [2(\frac{\sigma_{ij}}{r_{ij}})^9 - 3(\frac{\sigma_{ij}}{r_{ij}})^6] + \frac{1}{4\pi\varepsilon_0} \sum_{ij,nonbonded} \frac{q_i q_j}{r_{ij}} + \sum_{ij,bonded} k_{r,ij} (r_{ij} - r_{0,ij})^2 + \sum_{ijk,bonded} k_{\theta,ijk} (\theta_{ijk} - \theta_{0,ijk})^2.$$
(1)

In the right hand side of Eq. (1), the subscripts i, j, and k are the



Fig. 2. Schematic of the five silica surfaces used in the present study. (a) $SiO_2(OH)_{0,1}$, (b) $SiO_2(OH)_{1/2}$, (c) $SiO_2(OH)_{1/2}$, (d) $SiO_2(OH)_{1/2}$, and (e) $SiO_2(OH)_{2,2}$. (Note: $SiO_2(OH)_{1/2}$) means that each superficial silicon atom links to either one or two hydroxyl groups.).

atom indexes. The first term is the 9-6 Lennard-Jones potential describing van der Waals (vdW) interactions, where ε and σ represent the energy and distance parameters, respectively, and r is the interatomic distance. Coulombic potential in the second term is for electrostatic interactions, where q is atomic charge and ε_0 is the permittivity of vacuum. The harmonic potentials in the third and fourth terms are for bond stretching and angle bending interactions, respectively, where k, r, θ are the parameters of spring constant, equilibrium bond length and equilibrium angle. Meanwhile, the polymer consistent force field (PCFF) [23,24], which had been proved to reliably reproduce thermal transport properties of organic liquids and obtain simulation results in excellent agreement with experimental results [25,26], was used to model both triacontane and triacontanol molecules. More details about the force field parameters of simulation models can be inquired from Section S2 of the Supporting Information. As for interaction between silica and organic liquids, especial for the interaction force field at the interface, the 9-6 Lennard-Jones potential was used to describe the nonbonding interaction of *i*-th and *j*-th atoms, and the sixth power mixing rule was used to calculate parameters, which was defined as: $\varepsilon_{ij} = 2\sqrt{\varepsilon_i \varepsilon_j} \sigma_i^3 \sigma_j^3 / (\sigma_i^6 + \sigma_j^6)$ and $\sigma_{ij} = ((\sigma_i^6 + \sigma_j^6)/2)^{1/6}$ [27]. The cutoff radius was set as 12 Å for both nonbonding vdW and Coulombic real space interactions and the particle-particle-mesh (PPPM) algorithm with an accuracy of 1 \times 10⁻⁶ was employed to compute long range Coulombic interactions [28].

2.2. Simulation procedures

Each simulation case was conducted for a total duration of 30 ns and contained 3 phases: a 5 ns annealing process, a 15 ns nonequilibrium molecular dynamics (NEMD) process for imposing a stable heat flux at a given pressure, and a 10 ns NEMD process for collecting data. Periodic boundary conditions were applied in the x and y, but not in the z direction. Considering the fast vibrations of hydrogen atoms, a relatively small timestep of 0.5 fs was used, which was widely utilized in some previous works [29,30]. The simulation details are as follows.

In the annealing process, a 0.3 ns run of NEMD simulation followed by a 0.7 ns run of equilibrium molecular dynamics (EMD) simulation was repeated 5 times. Similar procedures have been commonly applied to minimize the energy of molecular configuration of polymers [31,32]. During the NEMD simulation, the temperature of the system rose from 395 K to 1000 K, was kept at 1000 K for 0.2 ns, and then dropped to 395 K, using a Nosé-Hoover thermostat with a damping coefficient of 50 fs, while two outmost silanol layers were fixed. Afterwards, the Nosé-Hoover thermostat was removed, and a 0.7 ns EMD simulation was conducted. The outmost left silanol layer remained fixed, whereas each oxygen atom in the outmost right silanol layer was subjected to a constant force in the *z* direction to control the pressure at 10 atm. The remaining outmost left and outmost right 672 silicon and oxygen atoms of silica acted as heat sink and heat source regions, with thickness of about 2 Å, and were respectively controlled at 370 K and 420 K using Langevin thermostats with a damping coefficient of 50 fs. These temperatures of heat sink and source regions were chosen to be between the melting point and boiling point of triacontane and triacontanol [33-36]. The NEMD simulation continued for 10 ns with the aim of relaxation. Next, we fixed the outmost right layer at its average position and performed an additional 5 ns NEMD simulation to ensure that the system reached a steady state. Lastly, it took 10 ns to collect and analyze data, where the simulation was divided into five time blocks to calculate the standard error of mean as the error bar [37].

2.3. Simulation analysis methods

Simulation analysis methods for interfacial thermal resistance (ITR) in Section 3.1, vibrational density of states (DOS) in Section 3.3, hydrogen bond in Section 3.4 and orientation of liquid molecules in Section 3.5 are illustrated in this section.

ITR is commonly utilized to characterize the performance of interfacial heat transfer, which is defined as:

$$ITR = \frac{1}{ITC} = \frac{\Delta T}{J_z} = \Delta T \frac{A}{dQ/dt},$$
(2)

where *ITC* refers to interfacial thermal conductance, J_z is heat flux in the *z* direction, ΔT is the temperature jump at the interface, *A* is the cross-sectional area of *x*-*y* plane, and dQ/dt is the energy input rate from a Langevin thermostat to the system, averaged over those for the heat sink and source. The temperature jump ΔT is calculated by extrapolating the linear fits of temperature profiles in the liquid and silica bulk regions to the interface. The position of solid–liquid interface locates at the center of the first number density peaks of silica and liquid closest to the interface.

Vibrational density of states (DOS) provides physical insights into the vibrational modes of various materials, which has been used to investigate interfacial heat transfer of solid–liquid interface in many previous studies [7,13,38] and can be calculated by taking the Fourier transform of the velocity autocorrelation function [39]:

$$G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-i\omega t} \frac{\langle v(t)v(0) \rangle}{\langle v(0)v(0) \rangle} dt,$$
(3)

where $G(\omega)$ is the DOS at an angular frequency ω , v(t) is atom velocity at time *t*, and the angle bracket denotes the ensemble averaging.

Lifetime of hydrogen bond is an indicator of its stability and strength, which is described by the hydrogen bond time correlation function [40], C(t), as follows:

$$C(t) = \frac{\langle h_i(t)h_i(0)\rangle}{\langle h_i(0)h_i(0)\rangle},\tag{4}$$

where $h_i(t)$ equals to 1 when a hydrogen bond exists at time t for the *i*-th pair of donor-acceptor, otherwise $h_i(t)$ equals to 0. Thus, C(t) describes the survival probability of a particular hydrogen bond during time t. The angle brackets denote an average over all donor-acceptor pairs and different time origins.

The orientation order parameter P(z), which is usually used to describe the orientational ordering of molecules [41], can be identified as:

$$P(z) = \frac{3}{2}\cos^2\theta_{s_1-s_2}^z - \frac{1}{2},$$
(5)

where $\theta_{s_1-s_2}^z$ means the angle made by the connecting line of two atomic sites s_1 and s_2 with the *z*-axis direction, which is vertical to the silica surface. The sites for a triacontane molecule are carbon atoms, and the sites for a triacontanol molecule include oxygen atom of hydroxyl group and carbon atoms. As Eq. (5) indicates, the value of P(z) ranges from -0.5 to 1: a negative value specifies that the molecular chain is oriented perpendicular to the interface normal direction; zero value represents that the molecules are oriented randomly; and a positive value indicates that the molecular chain is oriented parallel to the interface normal direction.

3. Results and discussion

3.1. Characteristics of interfacial heat transfer

Temperature and density distributions are displayed in Fig. 3 for three systems. Four key points should be highlighted from Fig. 3.

First, for all cases, the temperature jump at the cold side is always smaller than that at the hot side. Similarly, the number density of liquid at the cold side is larger than those at the hot side. Second, for the same silica surface, the temperature jumps at cold and hot sides of a silica-triacontane system are always larger than those at cold and hot sides of a silica-triacontanol systems, respectively. Third, a clear reduction in temperature jump can be observed when silica surfaces are covered with silanols, both for silica-triacontane and silica-triacontanol systems. However, an increase of surface silanol area number density does not significantly decrease the temperature jumps at silica-triacontane interfaces, whereas it further diminishes the temperature jumps at silicatriacontanol interfaces. Lastly, temperature gradients in the nearwall triacontanol liquids at the cold side are smaller than those in the middle bulk liquid regions in case of hydroxylated silica surfaces, but this phenomenon cannot be observed at the hot side of the same systems. As discussed above, we deduce that interfacial heat transfer mechanisms at silica-triacontane interfaces are different from those at silica-triacontanol surfaces, and temperature can influence interfacial heat transfer.

Fig. 4(a) and (b) show the results of ITR for silica-triacontane and silica-triacontanol systems, respectively. The results show that in general, ITR of silica-triacontane systems are higher than those of silica-triacontanol systems, and ITR at the cold side are smaller than those at the hot side. From the general understanding, ITR at solid-liquid interfaces is inversely correlated to the affinity of solids and liquids or wettability [40,42,43]. Because polar surfaces have higher affinity with polar liquids than non-polar liquids [44,45], ITR is lower for alcohol than alkane liquids. Furthermore, for both silica-triacontane and silica-triacontanol systems, ITR decreases sharply when silica surfaces are hydroxylated. However, more silanols at silica surfaces do not result in further reduction of ITR at silica-triacontane interfaces but do so at silica-triacontanol interfaces. It is worth mentioning that for silica-triacontanol systems, ITR at the cold side can be negative. This is because that we used the temperature distribution of bulk triacontanol to extrapolate the triacontanol temperature at the interface, but a non-linear temperature distribution of triacontanol occurred near the interface, which made us obtain an abnormal interfacial temperature of triacontanol and resulted in the negative ITR. The interpretation for this phenomenon and an alternative definition of ITR will be discussed in Sections 3.4-3.6.

3.2. Analysis of interfacial potential energy

Interfacial potential energy has played a significant role in explanation of ITR values in many works [5,44]. Here, interfacial potential energy was calculated as the total interaction energy between the solid atoms and liquid molecules divided by the x-y cross sectional area. In general, low interfacial potential energy means close interactions between the solid and liquid molecules, which results in higher heat transfer across the interfaces. As shown in Fig. 4(c), interfacial potential energy of any silica-triacontane system is always larger than that of the silica-triacontanol system of the same silica surface types. Meanwhile, interfacial potential energy at the cold side is smaller than that at the hot side, which can explain the ITR results of silicatriacontane systems in Fig. 4(a) that ITR at cold side is lower that at hot side. From Fig. 4(c) we can conclude that the silanol density has weaker influence on the interfacial potential energy of silica-triacontane systems, both at the cold and hot sides. In contrast, for silica-triacontanol systems, the surface modification with silanols dramatically decreases interfacial potential energy, which is approximately consistent with the change in ITR. The difference in the role of silanol density between silica-triacontane and silicatriacontanol interfaces should be attributed to the different hydro-



Fig. 3. Distribution of temperature and liquid number density for different silica surfaces: (a) SiO₂(OH)₀, (b) SiO₂(OH)₁, and (c) SiO₂(OH)₂, where the area density of surface silanols is also shown. The liquid is triacontane (upper panels) or triacontanol (lower panels).

gen bond capability between the triacontane and triacontanol. This point will be discussed specifically in Section 3.4. Fig. 4(d) displays the result of interfacial potential energy versus ITR for both silica-triacontane and silica-triacontanol systems. For the silicatriacontanol system, ITR tends to decrease when the interfacial potential energy decreases, which has been pointed out in a series of previous studies [12,44,46]. However, for the silica-triacontane system, the interfacial potential energy hardly changes when ITR varies. In summary, ITR at silica-triacontanol interfaces can be well-described by interfacial potential energy, but ITR at silicatriacontane interfaces is likely governed by other mechanisms.

3.3. Analysis of vibrational density of states

Fig. 5 shows DOS results of SiO₂(OH)₀-triacontane/triacontanol, SiO₂(OH)_{0/1}-triacontane/triacontanol and $SiO_2(OH)_2$ triacontane/triacontanol systems, with 0, 2.4, and 9.4 nm⁻² surface silanol density, respectively. The DOS profiles of bulk silica, silanols and triacontane/triacontanol are calculated separately. As DOS results at the cold side and hot side are similar, only DOS results at the cold side are shown in Fig. 5. DOS of triacontane and triacontanol are similar, since the two molecules differ only by a hydroxyl group, whose mass is relatively small, and its DOS can be drowned out by DOS of the remaining hydrogen and carbon atoms. In Fig. 5(a), when silica surfaces are not silanol-modified, the DOS profiles of silica and triacontane/triacontanol show a small overlap area, and this large vibrational mismatch results in the large ITR of both silica-triacontane and silica-triacontanol systems (Fig. 4(a) and (b)). As shown in Fig. 5(b), silanols can bridge the DOS profiles between silica and triacontane/triacontanol: At the frequency less than 20 THz, vibrational modes of silanols match well with those of bulk silica; at the frequency ranging from 20 THz to 40 THz, vibrational modes of silanols match well with those of triacontane/triacontanol. Thus, a formation of an efficient heat path from bulk silica to silanols to triacontane/triacontanol is expected. Such "vibration matching" effect leads to the substantial drop in the ITR in Figs. 4(a) and (b) from $SiO_2(OH)_0$ -triacontane/triacontanol system to SiO₂(OH)_{0/1}-triacontane/triacontanol system. However, comparing Fig. 5(b) and (c), increasing area number density of surface silanol groups cannot further significantly change characteristics of DOS of silanols, and therefore, ITRs of silicatriacontane systems from $SiO_2(OH)_{0/1}$ surface to $SiO_2(OH)_2$ surface, with silanol area number density increasing, do not show definite changes. To quantitatively assess the degree of vibration matching, the overlap area results for DOS of bulk silica, triacontane/triacontanol and silanols were calculated, which were listed in section S3 of the Supporting Information. Consequently, the ITR reduction for silica-triacontanol systems from SiO₂(OH)_{0/1} surface to SiO₂(OH)₂ surface, with silanol area number density increasing, should be attributed to other heat transfer mechanisms than vibration matching, such as interfacial potential energy (Section 3.2) and hydrogen bond formation (Section 3.4). In addition, it is worth mentioning that for the triacontanol systems, the ITR of unmodified surface (SiO₂(OH)₀) of 72.8(hot side)/56.9(cold side) K m^2 GW⁻¹ was reduced to 13.8(hot side)/3.2(cold side) K m^2 GW⁻¹ and 6.8(hot side)/-4.3(cold side) K $m^2\ \text{GW}^{-1}$ by the surface modifications of $SiO_2(OH)_{0/1}$ and $SiO_2(OH)_2$ types, respectively, which means over 80% reduction of ITR is likely due to the vibration matching. The triacontane systems show similar ITR reduction by the silanol modifications, though the amount of reduction is less than those for the triacontanol systems.

3.4. Analysis of hydrogen bonds

As discussed in Section 3.3, for the interfacial heat transfer between silica and triacontane, which is hydrogen bond incapable, vibrational mode matching is dominant in determining ITR decrease. On the other hand, for the hydrogen bond capable liquid, under no circumstances can the effect of the formation of hydrogen bonds be ignored in the interfacial heat transfer. Here, we conducted the analysis of hydrogen bonds for silica-triacontanol systems. As shown in Fig. 6(a), hydrogen bonds are typically identified via the geometric criteria [19]: in our definition, the donoracceptor distance (r_{DA}) must be less than 4 Å, and the donor-



Fig. 4. (a) Interfacial thermal resistance (ITR) of diverse silica-triacontane systems; (b) Interfacial thermal resistance of diverse silica-triacontanol systems; (c) Interfacial potential energy of diverse silica-triacontane and silica-triacontane systems; (d) Interfacial potential energy versus interfacial thermal resistance for diverse silica-triacontane and silica-triacontane systems; (d) is used to help show the inverse proportional relationship between interfacial potential energy and ITR of silica-triacontanol systems.



Fig. 5. Vibrational density of states (DOS) for systems of (a) $SiO_2(OH)_0$, (b) $SiO_2(OH)_{0/1}$, and (c) $SiO_2(OH)_2$. The liquid is triacontane (upper panels) or triacontanol (lower panels). As DOS results at the cold side and hot side are similar, only DOS results at the cold side are shown in Fig. 5.

hydrogen–acceptor angle (θ_{DHA}) must be greater than 140°. There are three possible donor–accepter pairs that have significant effect on interfacial hat transfer: silanol–alcohol, alcohol–silanol, and silanol–silanol, which are respectively named as hydrogen bonds (H-bonds) of (Si)OH–O(C), (Si)O–HO(C) and (Si)OH–O(Si). The anal-

ysis of hydrogen bonds is divided into two parts: number of hydrogen bonds and lifetime of hydrogen bonds.

3.4.1. Number of hydrogen bonds

Fig. 6(b) shows the average number of hydrogen bonds between triacontanol and diverse silica surfaces. Hydrogen bonds be-



Fig. 6. (a) Different types of hydrogen bonds in this work with the geometry for hydrogen bond criteria; (b) Average number of hydrogen bonds of diverse silica-triacontanol systems; (c) Interfacial potential energy versus the number of hydrogen bonds between silica and triacontanol for silica-triacontanol systems; (d) Effective hydroxyl density of diverse silica surfaces for silica-triacontanol systems; (e) Interfacial thermal conductance versus the hydroxyl density and effective hydroxyl density of silica surface for silica-triacontanol systems.

tween silica and triacontanol (ie. (Si)OH-O(C) and (Si)O-HO(C)) and Hydrogen bonds among silanols (ie. (Si)OH-O(Si)) are separately counted for both cold side and hot side. Two key points need to be pointed out. First, the average number of hydrogen bonds at the cold side is larger than that at the hot side for all cases, as expected from the less active thermal motion and larger density at the cold side. In addition, the difference in the number of hydrogen bonds between the hot and cold sides is larger for the silanol-triacontanol pairs than the silanol-silanol pairs, i.e., the former is more sensitive to temperature. Second, if surface silanol density is small, only a few hydrogen bonds form among silanols and a large number of hydrogen bonds forms between silanols and triacontanol. With the increase of surface silanol density, not only the average number of hydrogen bonds between silanols and triacontanol increases, but also the average number of hydrogen bonds among silanols tends to grow. For SiO₂(OH)₂ silica surface, the average number of hydrogen bonds among silanols can be even larger than that between silanols and triacontanol, which demonstrates that silanols and triacontanol are competing for hydrogen bonds formation. From this we conclude that increasing hydroxyl density of silica surface cannot linearly increase the average number of hydrogen bonds between silanols and triacontanol, nor does it always decrease the interfacial potential energy. Fig. 6(c) plots the number of hydrogen bonds between silanols and triacontanol versus the interfacial potential energy for silica-triacontanol systems. More hydrogen bonds between silanols and triacontanol can lead to the lower interfacial potential energy. Compared with the number of hydrogen bonds between silanols and triacontanol, the effect of temperature on the interfacial potential energy is negligible.

As discussed above, the formation of hydrogen bonds between silanols and triacontanol competes with the formation of hydrogen bonds among silanols as the hydroxyl density of silica surface increases. As a consequence, ITR does not decrease linearly with the increase of the hydroxyl density of silica surface ($\rho_{silanol}$), shown in Fig. 6(e). Xu et al. put forward that the effective hydroxyl density of silica surface (ρ_{eff}) is well-correlated with the interfacial heat transfer between silica surfaces and water [19]. Here, we apply this to our silica-triacontanol systems. The effective hydroxyl density of silica surfaces, ρ_{eff} , is defined as:

$$\rho_{eff} = \frac{N_{sil-alc}}{N_{total}} \rho_{silanol}, \tag{6}$$

where $\rho_{silanol}$ is the hydroxyl density of the silica surface, N_{total} is the total number of hydrogen bonds, and $N_{sil-alc}$ is the number of hydrogen bonds between silanols and triacontanol. As shown in Fig. 6(d), for each silica surface, effective hydroxyl density of silica surface with lower temperature is larger than that with higher temperature. With the increase of the hydroxyl density of the silica surface, effective hydroxyl density initially increases and fi-



Fig. 7. (a) Lifetime of hydrogen bonds in the SiO₂(OH)_{0/1}-triacontanol system; (b) Mean lifetime of hydrogen bonds for diverse silica-triacontanol systems; (c) Analysis of silica-triacontanol hydrogen bond conformations for diverse silica-triacontanol systems.

nally saturates, even slightly decreasing since more silanol-silanol hydrogen bonds form rather than silanol-triacontanol hydrogen bonds. Such variation of effective hydroxyl density strongly correlates with ITR in Fig. 4(b). Fig. 6(e) exhibits the dependence of interfacial thermal conductance (i.e. the reciprocal of ITR) on the hydroxyl density ($\rho_{silanol}$) and effective hydroxyl density (ρ_{eff}) of diverse silica surfaces, respectively. Take results at the hot side as an example, the hydroxyl density of silica surface and ITC are not linearly related, and the curve of ITC levels off when the hydroxyl density of silica surface is about 7 nm⁻² or higher. However, effective hydroxyl density and ITC show the excellent linear relationship at least for the hot side, which means that effective hydroxyl density, which takes the competitive relationship between hydrogen bonds between silanols and triacontanol and those among silanols into account, can more efficaciously predict the variation of ITC than the hydroxyl density of silica surface. In essence, larger effective hydroxyl density of silica surface means smaller ITR for silicatriacontanol systems. At the cold side, the correlation between the effective hydroxyl density and ITC is not clear because of the negative ITR, which is not shown in Fig. 6(e). However, as we will see in Section 3.6, a similar conclusion can be derived if we use the local ITR. Nevertheless, as shown in Figs. 6(e), temperature can influence the relationship between effective hydroxyl density and ITC, and we suspect that this is not only because of the number of hydrogen bonds but also because of the lifetime of hydrogen bonds.

3.4.2. Lifetime of hydrogen bonds

Fig. 7(a) depicts the evolution of C(t) over time for SiO₂(OH)_{0/1}triacontanol system, and other results can be seen in Section S4 of the Supporting Information. As in previous literature [47], we used the approximation $C(t) \sim \exp(-t/\tau)$, assuming that the breaking of hydrogen bonds occurs randomly with the mean lifetime τ . In Fig. 7(b), the mean lifetime τ by different types of hydrogen bonds is shown, whereas the difference in mean lifetime for the same type of hydrogen bond between the hot and cold sides is about 5~20 ps. The results show that for both silanol-triacontanol and silanol-silanol hydrogen bonds, a hydrogen bond tends to own longer lifetime at the cold side, and the weakening effect of higher temperature on the lifetime of silanol-triacontanol hydrogen bonds is more pronounced than that of silanol-silanol hydrogen bonds.

Furthermore, it needs to be pointed out that the mean lifetime for each hydrogen bond type is different for different silica surfaces and is not proportional to silanol density. Here, we propose that not only the temperature and the area number density of surface silanols, but also the arrangement style of surface silanols can affect the configurations of hydrogen bonds and thus affect the lifetime of hydrogen bonds. To examine this, we further analyzed the total number of silanol-triacontanol hydrogen bonds according to different molecular configurations as shown in Fig. 7(c). More than 90% hydrogen bonds are made up of five major hydrogen bonds configurations, which are named as (Si)O-HO(C),



Fig. 8. Orientation of near-wall organic liquids for (a) SiO₂(OH)₂-triacontane system, and (b) SiO₂(OH)₂-triacontanol system; (c) Effect of triacontanol orientation on the near-wall temperature distribution.

(Si)OH–O(C), (Si)O–HO(C)&(Si)OH–O(Si), (Si)OH–O(C)&(Si)O–HO(C), and (Si)OH–O(C)&(Si)O–HO(Si). For the first two configurations of hydrogen bond (type A hydrogen bond configuration), the oxygen in the silanol only acts as an acceptor or donor for a single hydrogen bond, and in the latter three configurations (type B hydrogen bond configuration), the oxygen in the silanol acts as both an acceptor and a donor simultaneously. The percentages of different configurations reveal that if more hydrogen bonds are of type A hydrogen bond configuration, the mean lifetime of hydrogen bonds will be shorter, which means type A hydrogen bond configuration is less stable than type B hydrogen bond configuration. This is easily understood since vibration of silanols can be constrained if one silanol forms two hydrogen bonds at the same time, which is beneficial to the stability of hydrogen bonds.

3.5. Analysis of orientation of liquid molecules

As discussed above, interfacial potential energy, vibration density of state, and hydrogen bonds have been demonstrated to explain the ITR variation of silica-triacontane and silica-triacontanol systems in Figs. 4(a) and (b). However, the different temperature gradient of the near-wall triacontanol liquids at the cold side from that in the bulk liquid region, as well as the negative ITR, have not been explained. Two points need to be stressed: (1) A temperature gradient of liquid in the near-wall region that is different from that in the bulk region only exists in the silica-triacontanol systems, but not in the silica-triacontane systems; (2) Even in the silica-triacontanol system, the difference in temperature gradient is only observed at the cold side, but not at the hot side. Here, the orientation of liquid molecules is analyzed to clarify these points.

Fig. 8(a) and (b) respectively display the profiles of the orientation order parameter in the $SiO_2(OH)_2$ -triacontane system and $SiO_2(OH)_2$ -triacontanol system. Other cases have similar P(z) distributions, as shown in the Section S5 of the Supporting Information. For SiO₂(OH)₂-triacontane system, the value of P(z) is negative in the region adjacent to the silica surface, which means that triacontane molecules prefer the orientation parallel to the interface. In contrast, for SiO₂(OH)₂-triacontanol system, the value of P(z) is positive in the region adjacent to the silica surface, which means that triacontanol molecules prefer aligning vertical to the silica interface. As the region moves away from the interface, the orientation of both triacontane and triacontanol molecules becomes isotropic and random, with $P(z) \approx 0$. Such distribution is commonly seen at interfaces between polymers and solids [40,48,49]. The vertical orientation of triacontanol molecules near the interface is likely due to the geometric constraints by hydrogen bonds with surface silanols. However, triacontane molecule does not prefer such vertical adsorption structure because the triacontane does not form hydrogen bonds with surface silanols. Fig. 8(c) compares the temperature distribution of triacontanol molecules in the SiO₂(OH)₂-triacontanol system and their orientation order parameter at the cold side. Firstly, the temperature gradient of bulk region is constant where the triacontanol molecular orientation is random. On the other hand, the vertically aligned triacontanol molecules near the silica surface at the cold side form a temperature gradient that is different from that of the bulk region. It is worth noting that the region of vertical interfacial orientation of triacontanol molecules is almost identical to the region of smaller temperature gradient in triacontanol molecules. Thus, it can be imaged that there is an efficient heat path at the cold side of silicatriacontanol interface, where the heat is initially transported from silanols to the nearby hydroxyl groups of triacontanols via hydrogen bonds, then from the hydroxyl groups to the backbones of triacontanols via intramolecular interactions, and finally to triacon-



Fig. 9. (a) Comparison between original and local interfacial thermal resistances for diverse silica-triacontane and silica-triacontanol systems; (b) Effective hydroxyl density versus local interfacial thermal conductance (local ITC) for diverse silica-triacontanol systems; (c) Summary of this work.

tanol molecules in the bulk region via intermolecular interactions, as shown schematically in Fig. 9(c). The vertical orientation of triacontanol toward the silica surface helps the heat to travel farther and more efficiently. The smaller temperature gradient, i.e., higher thermal conductivity, of triacontanol at the cold side is exactly the embodiment of the efficient heat transfer through intramolecular interactions in the molecular backbones, which are oriented parallel to the heat flux direction. As for silica-triacontane systems, triacontane molecules tend to lie on the silica surface and the efficient heat path discussed above cannot exist, and thus temperature gradients in the near-wall region and bulk region of triacontane liquids is similar. However, apart from silica-triacontane systems, different temperature gradients between the near-wall region and bulk region also cannot be observed at the hot side in silica-triacontanol systems though triacontanol molecules also prefer vertical orientation toward silica surface at hot side. Here, we suspect this is due to that higher temperature decreases the number and lifetime of silica-triacontanol hydrogen bonds, which results in the silanol-hydroxyl-alkyl heat path being unstable and the amount of heat through this path is limited. In addition, there may be some structural or dynamic differences that are not apparent from current analysis leading to this phenomenon at hot side. In any case, some future studies about such temperature effect are called for to give a full understanding.

In essence, the fundamental mechanism is that hydrogen bond acts as a bridge, and heat can be transferred via intramolecular interactions in the backbones of triacontanols. More hydrogen bonds forming and longer lifetime of hydrogen bonds are conducive to the interfacial heat transfer.

3.6. Local interfacial thermal resistance

As discussed in Section 3.5, temperature gradient in the nearwall region of the cold side, as well as the thermal conductivity, is different from that in the bulk region for silica-alcohol systems. Hence, it is possible to obtain the negative ITR (Fig. 4(b)) if the temperature distribution in the bulk region is extrapolated to calculate the interfacial temperature difference at the cold side. Furthermore, as discussed in Section 3.4.1, effective hydroxyl density and ITC in Fig. 6(e) show an excellent linear relationship at the hot side, whereas the negative ITR obscures this correlation at the cold side. In this section, we apply a local ITR that gives a clear correlation with effective hydroxyl density at both the hot and cold sides. To distinguish ITR mentioned in other sections from the local ITR, the former is named as the original ITR in this section. For the local ITR, the liquid temperature distribution in the region within 12 Å (the cutoff radius of simulation setting) from the interface is extrapolated to calculate the interfacial temperature difference.

Fig. 9(a) compares the local ITR and original ITR. For silicatriacontane systems, local ITR and original ITR are almost the same. For results of local ITR and original ITR at the hot side in silicatriacontanol systems, they are roughly equal. This is easily understood by the fact that temperature gradients in the near-wall region and bulk region are nearly equal. As shown in Fig. 8(c), smaller temperature gradient at the cold side in silica-triacontanol systems ensures that the extrapolated temperature of triacontanols is always greater than that of the silica surface, which makes the local ITR and original ITR at the cold side in silica-triacontanol systems are much different. Fig. 9(b) perfectly demonstrates the linear relationship between the local interfacial thermal conductance (local ITC) and effective hydroxyl density for silica-triacontanol systems. It is worth noting that the slopes of effective hydroxyl density versus the local interfacial thermal conductance at the cold and hot sides are different, which is likely to highlight the effects of temperature on the number and lifetime of hydrogen bonds.

4. Conclusions

In this work, we investigated the role of hydrogen bonds and interfacial heat transfer between diverse silanol hydroxylated silica surfaces and organic liquids using molecular dynamics simulations, where triacontane and triacontanol were chosen as hydrogen bond incapable and capable organic liquids, respectively. The surface modification by silanols significantly improves the interfacial heat transfer between silica and triacontane/triacontanol. It is the interfacial vibration matching but not the interfacial potential energy or the amount of silanol groups that determines the interfacial heat transfer between silica and hydrogen bond incapable triacontane, whereas the amount of silanol groups can further affect interfacial heat transfer in silica-triacontanol systems. In silicatriacontanol systems, more silanols generally means smaller ITR, though the effect is limited at higher silanol densities because silanol-silanol hydrogen bonds hinder the formation of silanoltriacontanol hydrogen bonds. Effective hydroxyl density, that only takes hydrogen bonds between silanol and liquid into account, is found to correlate well with the ITC. In addition, temperature also influences the interfacial heat transfer of silica-triacontanol systems because higher temperature lowers the number of hydrogen bonds and weakens the lifetime. Different arrangements of surface silanols result in different conformations of hydrogen bonds, which affects the lifetime of hydrogen bonds. Finally, orientations of hydrogen bond incapable and capable organic liquids are different, where triacontane prefers the orientation parallel to the interface, while triacontanol prefers aligning vertical to the silica surface. As a result, there was an efficient silanol-hydroxyl(Alco)-alkyl(Alco) heat path at the silica-triacontanol interface, which caused the interfacial molecular layers of triacontanol to have higher thermal conductivity.

Declaration of competing interest

There are no conflicts to declare.

CRediT authorship contribution statement

Haiyi Sun: Conceptualization, Methodology, Software, Visualization, Data curation, Writing - original draft, Writing - review & editing. Donatas Surblys: Conceptualization, Methodology, Software, Writing - review & editing. Hiroki Matsubara: Conceptualization, Methodology, Writing - review & editing. Taku Ohara: Conceptualization, Project administration, Writing - review & editing.

Data availability

Data will be made available on request.

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Supplementary materials

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