

# Electronic Supplementary Information: Microscopic Properties of Forces from Ice Solidification Interface Acting on Silica Surfaces Based on Molecular Dynamics Simulations

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## Parameters of water molecules and silica wall

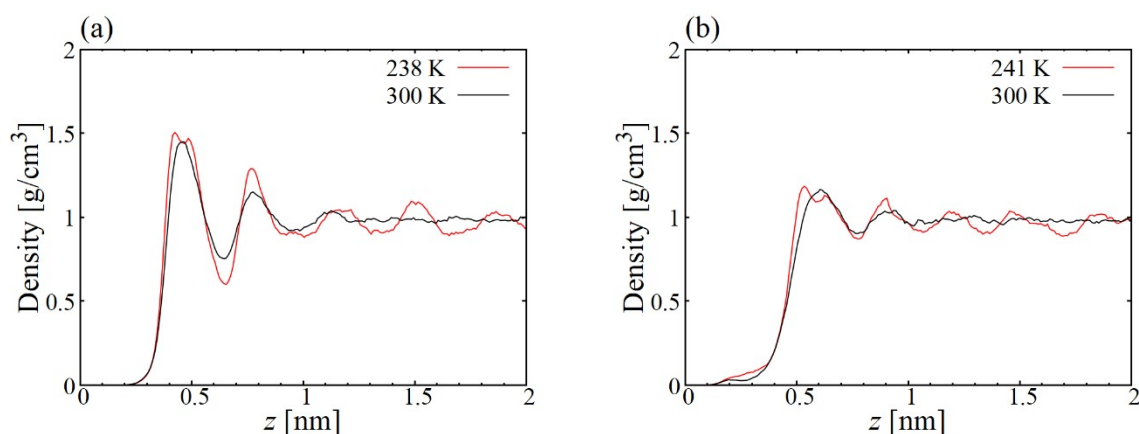
**Table S1.** Parameters of water molecules and silica wall.

Water molecules <sup>1</sup>	$\sigma$ Å	$\epsilon$ kcal/mol	$q$ C
H	0	0	0.5564
O	3.1589	0.1852	-1.1128

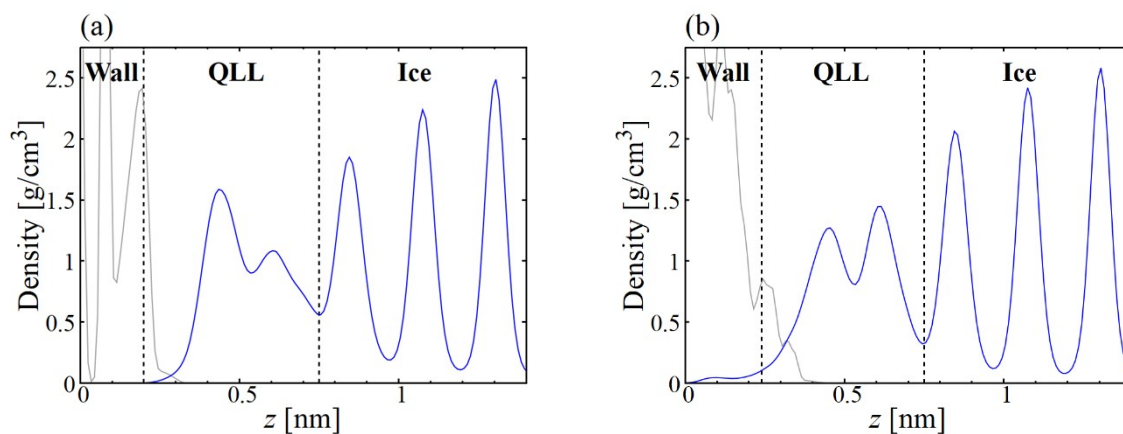
  

Silica <sup>2</sup>	$\sigma$ Å	$\epsilon$ kcal/mol	$q$ C
H	0	0	0.2216
O (silanol group)	3.21	0.228	-0.3601
Si (silanol group)	4.55	0.04	0.4669
O	3.21	0.228	-0.1899
Si	4.55	0.04	0.3798

## Density profiles of water molecules and silica walls



**Fig. S1** Density profile of water molecules in the direction perpendicular to the surface in a liquid state; (a) crystalline and (b) amorphous silica surface.

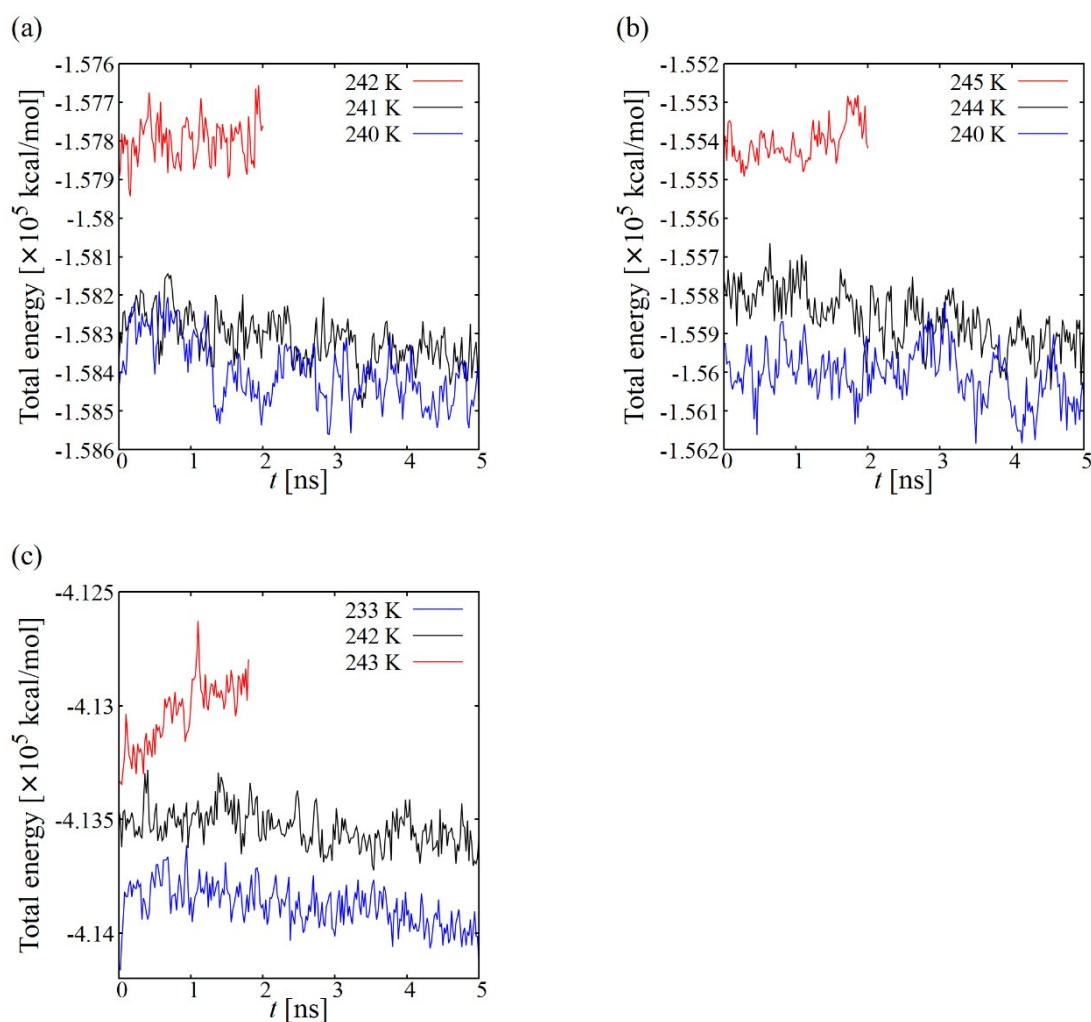


**Fig. S2** Density profile of water molecules (blue line) and silica walls (gray line) perpendicular to the surface in an ice state; (a) crystalline and (b) amorphous silica surface.

## Confirmation of the melting point

Figure S3 depicts the time evolution of the total energy (i.e., the sum of the kinetic and potential energies) at each controlled temperature. The total energy decreases under low-temperature conditions, which indicates that the potential energy of water molecules decreases owing to ice crystallization.<sup>3,4</sup> Conversely, the total energy increases under high-temperature conditions, which indicates the melting of ice.

Figure S3 indicates that the melting points in the calculation system of the crystalline silica plane (“flat crystalline”), amorphous silica plane (“flat amorphous”), and structured amorphous silica wall (“structured amorphous”) were 241, 244, and 242 K, respectively.



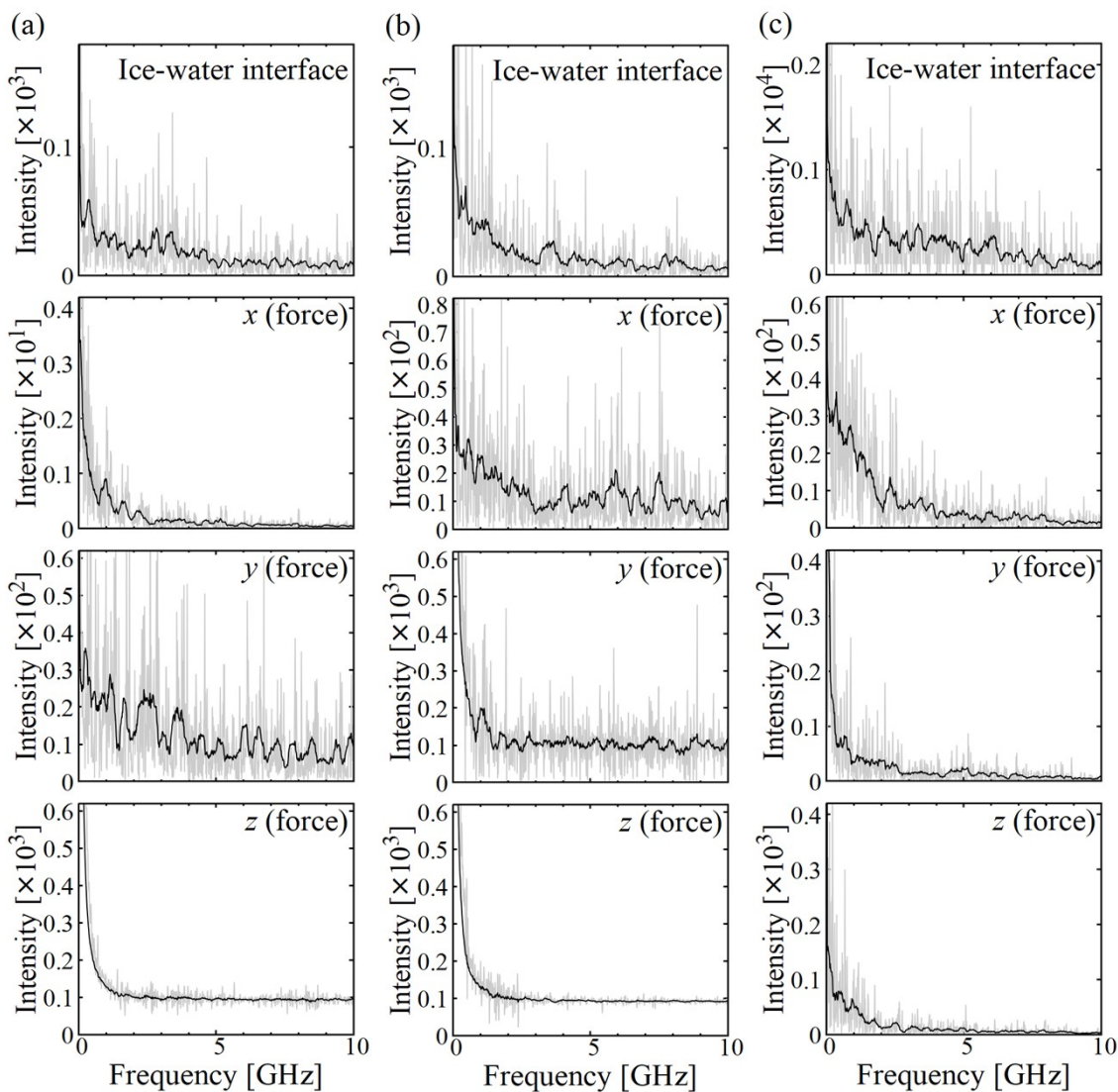
**Fig. S3** Time evolution of the total energy at each controlled temperature for the (a) flat crystalline, (b) flat amorphous, and (c) structured amorphous surfaces.

## **Spectral properties of the microscopic forces**

To investigate the spectral properties of the forces acting on the wall from water molecules, Fourier transforms were performed on the time evolutions of the forces on three types of silica walls. The output intervals of the force data were obtained every 0.01 ns, and the number of sampling data used for the frequency analysis was 10000. The data for the solidification interface fluctuations were obtained at intervals of 0.02 ns, and the number of sampling data was 5000. The frequency information obtained from these data is shown in Fig. S4.

In Fig. S4, both the fluctuation frequency at the solidification interface and the force acting on the wall from the water molecules have a distribution that increases in the low frequency band. In the high frequency band above 5 GHz, the intensity values are small, and no specific frequency peaks that are common to the frequency distribution of the solidification interface and the force can be confirmed. This spectral information implies that the fluctuations in the force at frequencies above 5 GHz are not caused by the fluctuations in the solidification interface. In the low–frequency range below 5 GHz, the solidification interface and the forces show similar frequency distributions. However, it is difficult to clearly identify the frequencies that are common between the solidification interface and the forces because the frequency distributions in the low–frequency range contain noise. Nevertheless, these results indicate that the effects of the solidification interface may be observed in the frequency band below 5 GHz, thus indicating that fluctuations in the higher frequency band can be eliminated to observe the effects of the solidification interface.

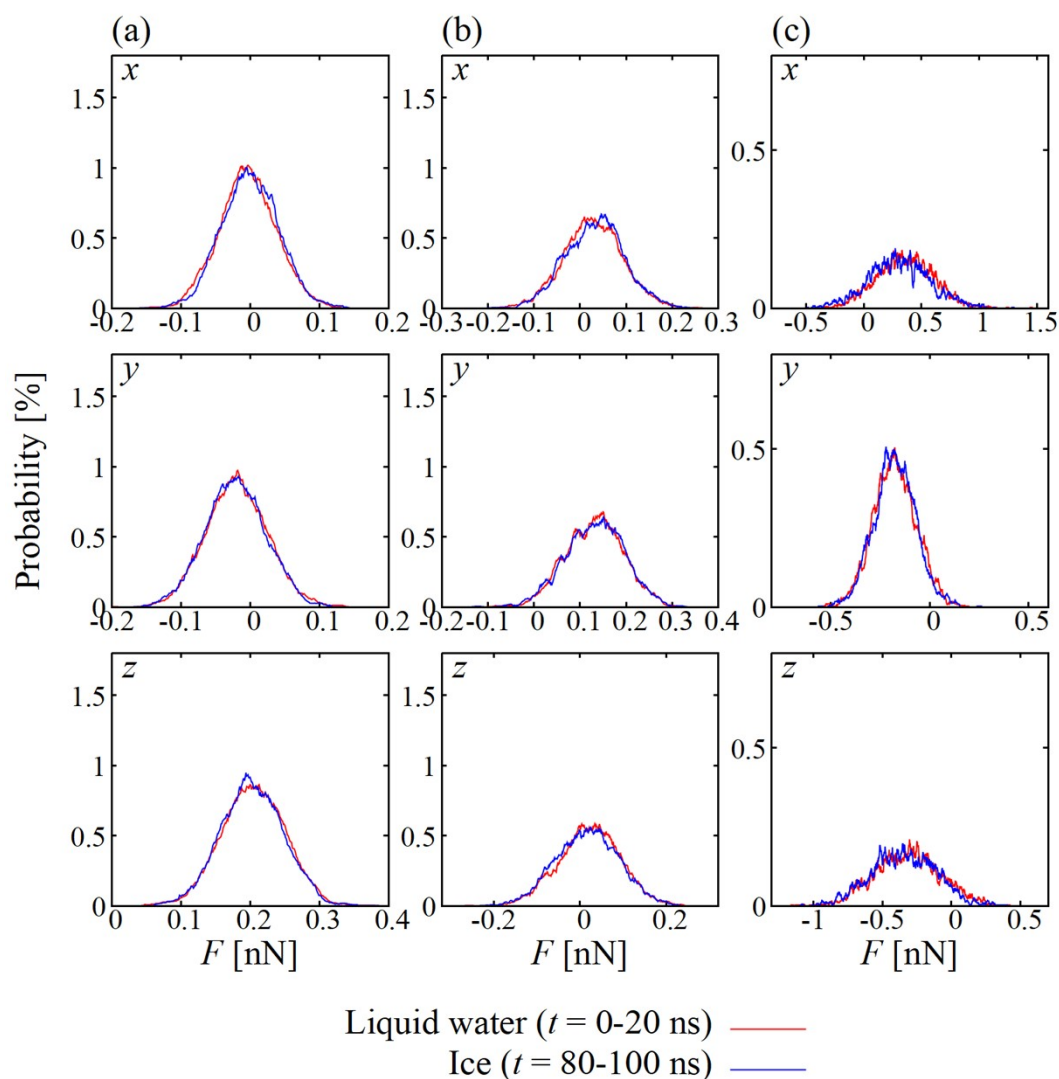
From the above, the force fluctuations at frequencies below 4 GHz (0.25 ns) were eliminated by time averaging.



**Fig. S4** Frequency distributions for the ice–water interface and forces from water molecules to the walls for the (a) flat crystalline, (b) flat amorphous, and (c) structured amorphous surfaces.

## Probability distributions of the forces

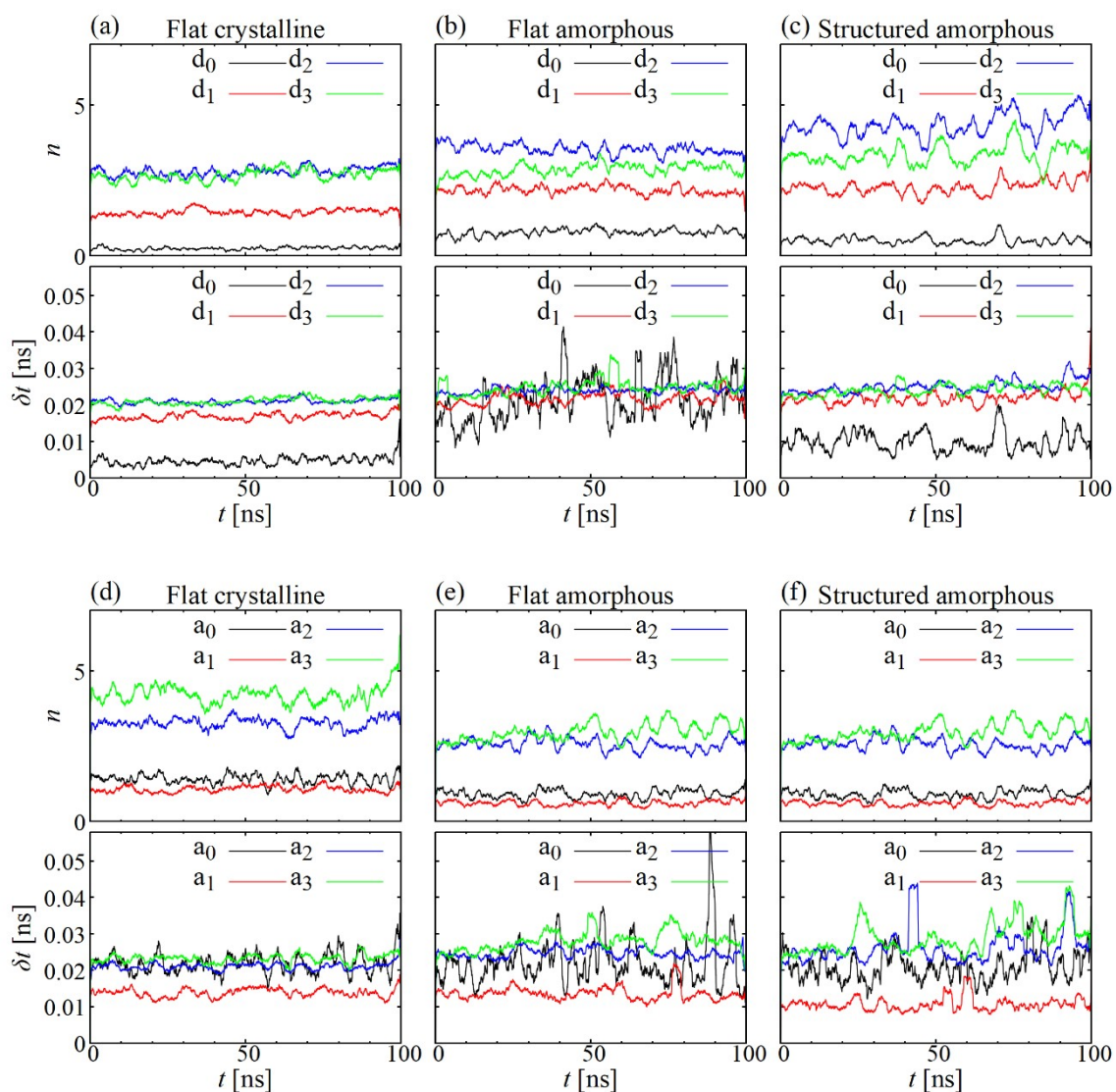
The probability distributions of the 0.01 ns averaged forces are shown in Fig. S5. The probability distributions of the forces acting on the three types of silica walls along each  $xyz$  direction presented little changes before and after solidification. In particular, this figure with the range of force distributions displayed on the  $x$ -axis does not clearly show the difference before and after the solidification compared to Fig. 5 in the main manuscript.



**Fig. S5** Probability distributions of the microscopic forces from water molecules acting on the silica surfaces for the (a) flat crystalline, (b) flat amorphous, and (c) structured amorphous surfaces. The forces used to calculate the distribution functions were averaged at 0.01 ns.

## Hydrogen bonds between water molecules and silanol groups

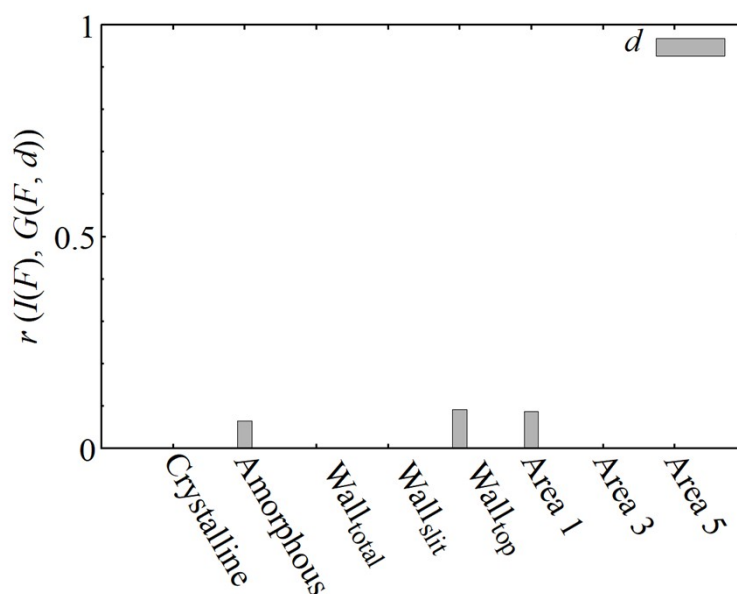
Figure S6 depicts the time evolutions of  $n$  and  $\delta t$  for each hydrogen bond type. It can be observed that  $n$  does not vary significantly upon contact between the solidification interface and the wall surface in any case. In contrast,  $\delta t$  fluctuates significantly throughout the calculation regardless of the solidification, particularly for  $a_0$  and  $d_0$ . This occurs because  $a_0$  and  $d_0$  formed hydrogen bonds with the silanol groups and are easily converted to other types of hydrogen bonds. Consequently, the  $\delta t$  values for  $a_0$  and  $d_0$  exhibit larger fluctuations than those of the other hydrogen bond types during the calculation.



**Fig S6** Time evolutions of  $n$  and  $\delta t$  on silica surfaces for (a–c) donors and (d–f) acceptors. The lines indicate the type of hydrogen bonds based on Fig. 6.

### Correlation between forces and thickness of the layer at silica–ice interface

The correlation between the minimum position of the ice crystals  $d$  (shown in Fig. 3) and microscopic forces was investigated, as shown in Fig. S7. We confirmed that the correlation between  $d$  and the forces is smaller than that between the hydrogen bonds and the forces, as shown in Fig. 9. This is because the solidification induced changes in the forces occur over a shorter period, whereas the ice crystals are distinguished by hydrogen bonds that are maintained for 2 ns.



**Fig. S7** Correlations between forces from water molecules acting on silica walls and layer thickness at silica–ice interface  $d$ .

### REFERENCES

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2. T. J. Hou, L. L. Zhu and X. J. Xu, *J. Phys. Chem. B*, 2000, **104**, 9356–9364.
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