Supporting information

for

Structure of Ice Confined in Silica Nanopores

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S1. Methods

The silica pores are modeled using ClayFF forcefield proposed by Cygan et al.[1] using the parameters impeded in **Table S1**. ClayFF forcefield does not account for the bonded parameters in the silica surface, except for the surface OH bond stretching and the OH bond length is 0.1 nm. Once we protonated the nonbridging oxygens on the cleaved pore surface, we optimized the pore separately to obtain the equilibrium structure before the solvation with water. The number of water molecules required to reach 1 g/cm^3 was calculated based on the volume of each pore (V_P). The pore volume was calculated as follows:

$$V_P = \pi r^2 h \tag{1}$$

Where r is the pore radius, and h is the pore length in the z-direction (the direction parallel to the pore length). It is worth mentioning that h is infinite due to the periodic boundary conditions and thus, some properties have a negligible dependence on r compared to h such as the diffusivities.

Table S1. LJ parameters and the charges for atomic species of silica and TIP5P water model taken from Cygan et al.[1] and Mahoney and Jorgensen[2], respectively.

Atom	Description	σ (nm)	ε (kJ/mol)	q (e)
Parameters for Silica				
Si	Silicon atom	0.33020	7.7006×10^{-6}	2.1000
O_b	Bridging oxygen	0.31664	0.650190	-1.0500
O_h	Nonbridging oxygen	0.31664	0.650190	-0.9500
H	Hydrogen	0.00000	0.000000	0.4250
Parameter for TIP5P water				
O	Oxygen	0.31200	0.669440	0.0000
H	Hydrogen	0.30970	0.744752	0.2410
LP	Virtual site	0.00000	0.00000	-0.2410

σ is the finite distance at which the interatomic potential is zero.

ε is the depth of the potential well.

q is the atomic charge.

Once the solvated pores are optimized, simulated annealing protocol implemented in GROMACS 2018 was utilized to study the confined water properties at different temperatures. The reference temperature was applied to all the atoms in the systems by considering the silica atoms and water atoms as one group. Periodic annealing was used with 24 annealing points that state the time of the beginning and the end of each of the 12 temperatures points **(see Figure S1)**. Each system was equilibrated at 300 K for 10 ns and quenched to 183 K followed by systematic heating to 300 K with 10 ns equilibration time at each temperature.
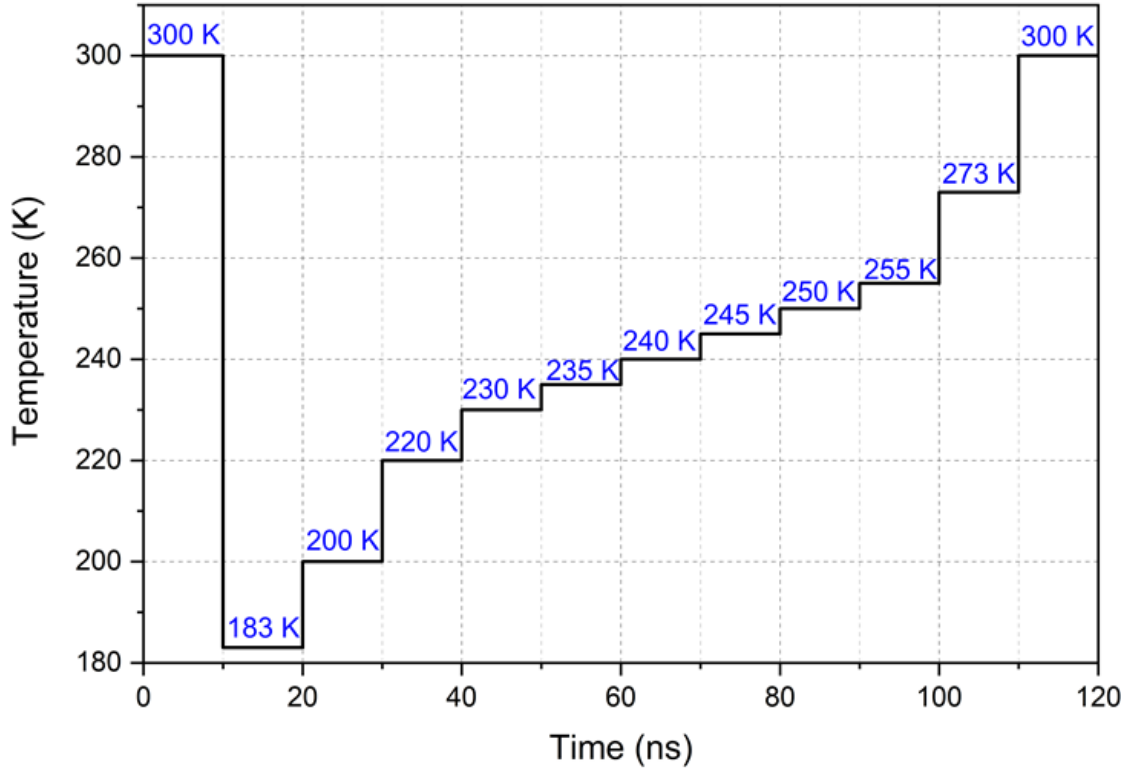
Figure S1. The temperature change algorithm with the simulation time of the water confined in 4 nm, 6 nm and 8 nm silica pores.

S2. Data analysis

S2.1. WAXS peaks fitting

The main peaks in the WAXS curves were fitted using Lorentzian function to probe the full width half maximum (fwhm) with the temperature change (**Figure S2**) as follows:

$$I = I_o + \frac{2A}{\pi} \frac{w}{4(Q - Q_c)^2 + w^2} \tag{2}$$

Where I is the intensity, I_o is the intensity background, A is the peak area, Q is the wave vector, Q_c is the peak center and w is FWHM. The thick transparent line represents the standard deviations obtained from the peaks fitting. The FWHM profiles show a steady behavior at temperatures below 255 K then dropped significantly to 0 at 300 K, which indicates the first-order transitions occur on heating the system from 255 K to 273 K and from 273 K to 300 K.
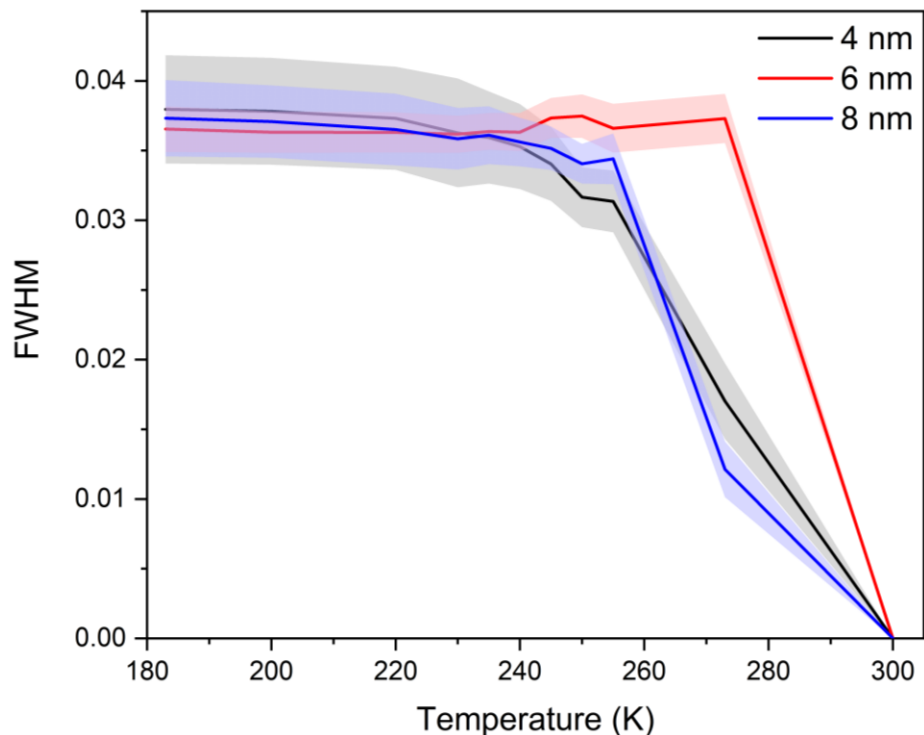
Figure S2. The Lorentzian full width half maximum of the WAXS main peaks as a function of the temperature applied on the water confined in 4 nm, 6nm and 8 nm silica pores. The transparent broad lines represent the standard deviation governed from the peaks fitting.

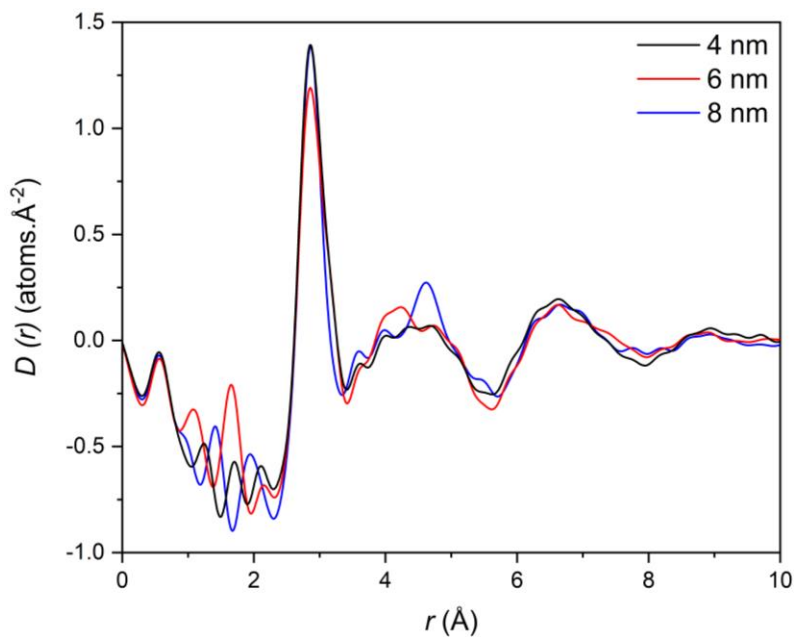**S2.2. The x-ray differential pair distribution function**

Figure S3. The x-ray differential pair distribution function ($D(r)$) of water confined in 4 nm, 6 nm, and 8 nm sized pores at 300 K.

S2.3. The pore-water radial distribution function

The interaction of the interfacial water layer with the hydroxyl groups on the pore surface was further analyzed by calculating the OH_{silica}-O_{water} radial distribution function as a function of the pore diameter and the temperature (**Figure S4**). The packing of the interfacial water layer around the surface OH is decreased with the increase of the temperature and the pore diameter.
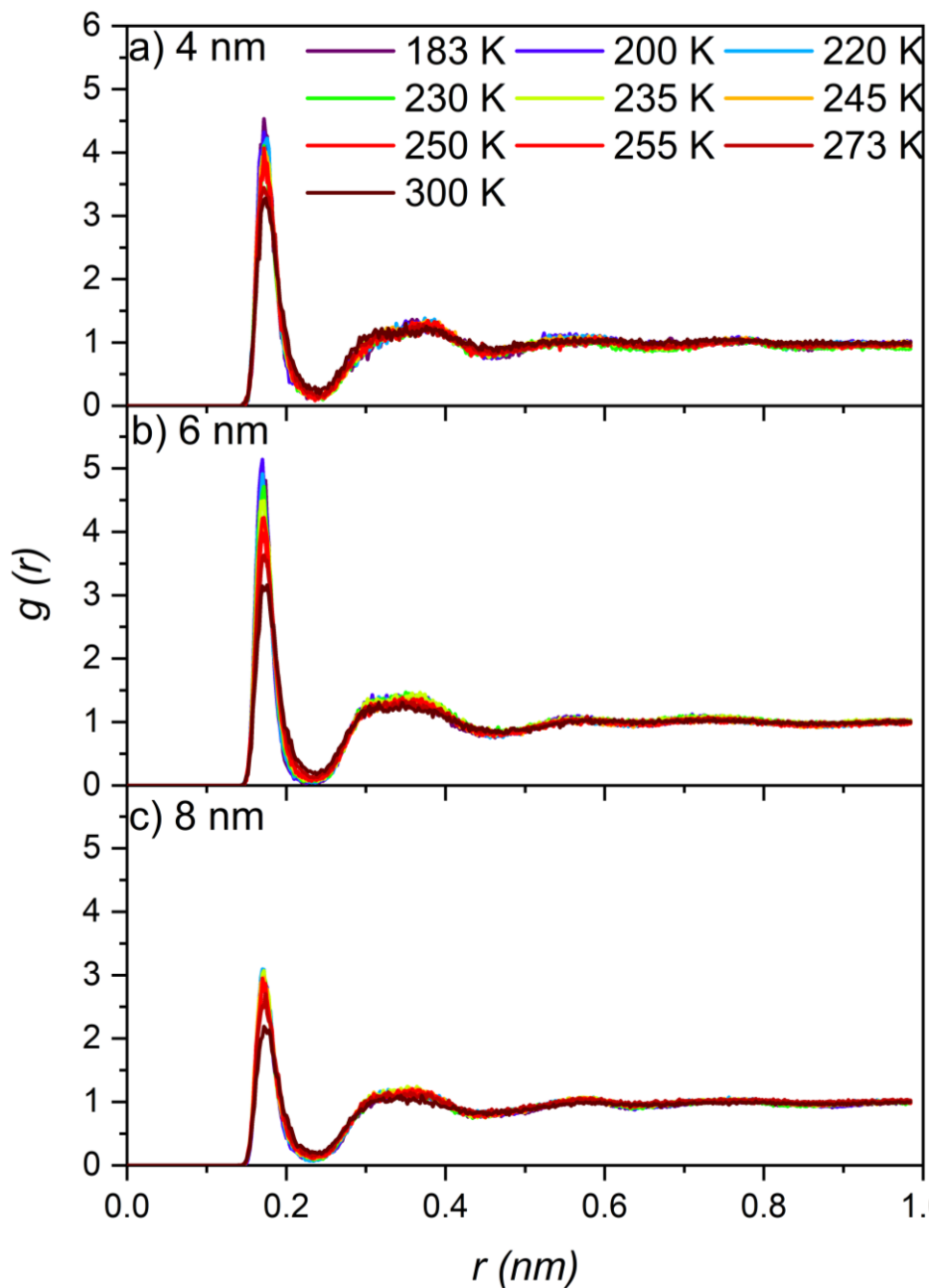

Figure S4. The radial distribution function of the OH group on the silica surface and the oxygen atom in the water molecules in 4 nm (a), 6 nm (b) and 8 nm (c) silica pores as a function of the temperature.

S2.4. Water-Water Hydrogen bonding

The hydrogen bonding lifetime **(Figures S5)** were calculated to obtain further insights on the formed water structures and their evolution as the temperature change. The hydrogen bonding lifetime was averaged over the entire 10 ns of each temperature of the water confined in 4 nm, 6 nm and 8 nm pores. Long-lasting hydrogen bonds are exhibited at the low temperatures that decrease to about 0.003 ns as the transition from solid to liquid phase occurs.
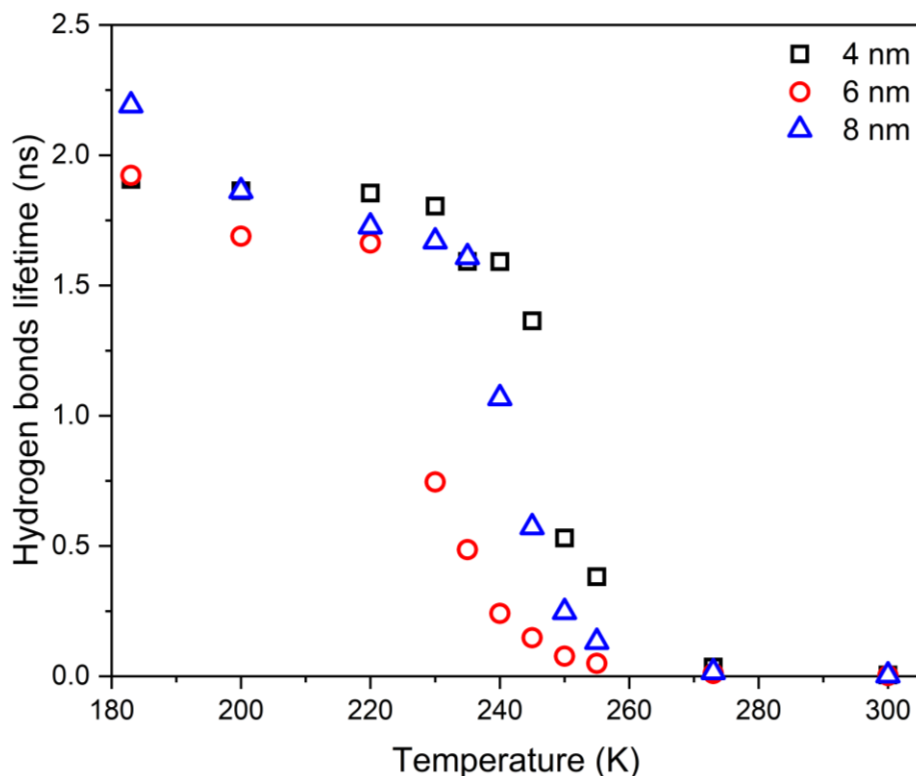

Figure S5. The average lifetime of the hydrogen bonds formed between water molecules confined in 4 nm, 6 nm and 8 nm silica pore as a function of the temperature. The lifetime was averaged over the entire 10 ns at which the system was equilibrated at each temperature.

S2.5. The mean square displacement of water

The mean square displacements **(Figure S6)** were calculated and used to estimate the self-diffusion coefficient of water as a function of the temperature and the confinement environment. The mean square displacement exhibited different profiles at low and high temperatures that is consistent with the solid-liquid phase transition of water. The mean square displacement was calculated in the direction parallel to the pore length due to the negligible length of the pore radius compared to the pore length.
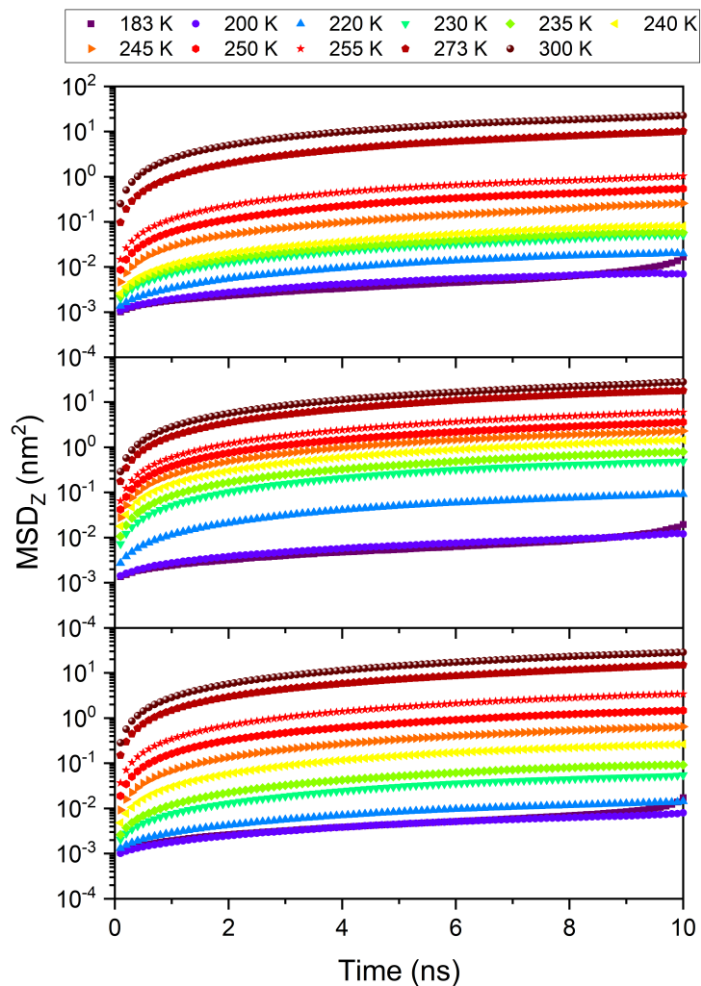
Figure S6. The mean square displacement of water confined in 4 nm, 6 nm and 8 nm silica pores as a function of the temperature.

References

1.   R. T. Cygan, J.J. Liang, A.G. Kalinichev, *J. Phys. Chem. B,* 2004**, 108**, 1255-1266.
2.   M. W. Mahoney, W.L. Jorgensen, *J. Chem. Phys.,* 2000**, 112**, 8910-8922.