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Water Confined in Cylindrical Pores: A Molecular Dynamics Study

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Abstract

Molecular dynamics simulations of water confined in two hydrophilic cylindrical pores—PH and PL—that differ in their silanol surface concentration (7.6 and 3.0 nm^{-2} , respectively) have been performed at 300 K . A strong interaction of interfacial water molecules with the pore was systematically found and gives rise to a layering effect, a significant distortion of both the hydrogen bond network (HBN) and the tetrahedral structure of these water molecules, and a corresponding subdiffusive mean square displacement along the main axis of the pores. By contrast, water molecules in the inner part of both pores were found to behave similarly to bulk water. The HBN and the tetrahedral configuration of water were more gradually distorted in the PL pore given the larger heterogeneity and rugosity of the surface, and the number of water–pore hydrogen bonds did not scale linearly with the silanol surface concentration of the pores, in part because of the close proximity between silanols in the PH pore. With the PL pore, the dynamic slowing down of water was found consistent with the experiment, suggesting that it provides a better model for the cylindrical MCM-41 mesopores. The structural and dynamical properties of water vary little with the silica force field.

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Keywords

Water; Confinement; MCM-41; Silica; Hydrogen bonds; Hydrogen bond network; Dynamics; Silanol surface concentration; Simulation

Introduction

Finding water in confined environments is by no means exceptional. A significant amount of water is indeed confined in porous materials, membranes, glasses, and minerals used in various industrial processes such as filtration and sorption, petrochemical refining, nuclear waste disposal, or heterogeneous catalysis. Recently, the remarkable advances in the tailoring of nanoporous materials—and more particularly in the control of pore size, dimensionality, and surface chemistry—have allowed the development of promising biotechnological applications like DNA sequencing or controlled release of pharmaceuticals, genes, or chemicals in which confined water plays a major role.^{1,2} A detailed understanding of the behavior of confined water is therefore fundamental.

Experimental and numerical studies have clearly established that the properties of interfacial water, also referred to as biological or hydration^{3–5} water, differ significantly from those of bulk water.^{6–8} In the particular case of MCM materials² with hydrophilic cylindrical pores with diameters of a few nanometers, the tetrahedral hydrogen bond network (HBN) of water, the melting/freezing temperature, and the diffusion coefficient are significantly affected due to the well-documented combination of finite size effects, change of dimensionality, and surface interactions.^{9–11} In the specific cases of crystalline and planar silica, numerical studies have demonstrated the strong effect of the silanol surface concentration on the structural, dynamical, and thermodynamical properties of water.¹² However, in the case of water confined in amorphous silica or in cylindrical silica nanopores, the variations of the confinement properties with changes in the silanol density which accompany the thermal treatment have not been thoroughly addressed^{13–25} (Figure 1).

The aim of the present work is to report the results of a numerical simulation study of confined water in two model cylindrical silica pores to investigate the influence of the silanol surface density on the structural and dynamical properties of water. For this purpose, two hydrophilic pores, with a diameter of about 3 nm were built with high and low silanol surface densities, 7.6 and 3.0 OH/nm², respectively, referred to here as PH and PL. The structural and dynamical effects of the silanol surface concentration on water properties have been characterized through local densities, hydrogen bonds, tetrahedral order parameter, and mean square displacement. The dependence of water properties on the force field used to represent silica in the simulations was also investigated.

Simulation Details

All simulations were performed using the CHARMM program²⁶ in the microcanonical (N , V , E) ensemble, where the number of atoms N , the volume V , and the total energy E of the system are constant. The periodic boundary conditions were only applied along the Z direction. The lengths of covalent bonds involving hydrogen atoms were kept fixed using the SHAKE algorithm²⁷ and a 1 fs timestep was used to integrate the Newton equations of motions with the Verlet leapfrog algorithm.²⁸ An atom-based force-switching function²⁹ was employed to smoothly switch van der Waals (vdW) forces to zero between 14 and 16 Å, whereas electrostatic forces were shifted to zero at 16 Å with an atom-based force-shifting function.²⁹ The PH and PL pores were generated and filled following the procedures described in the Supplementary Materials. Water molecules were represented by the rigid SPC/E model,³⁰ and the silica pore atoms by the Brodka force field.³¹ The silica frame was

kept rigid by freezing the positions of the O and Si atoms while rotations of the H atoms around the Si–O bonds were allowed. The size of the box was 57.0584 Å, and the O–H distance was kept fixed at 0.95 Å using the SHAKE algorithm.²⁷ Because the valence parameters are lacking in the Brodka force field, the Si–O–H angle was also constrained at 116° with a force constant of 5,000 kcal/mol Å² using the MMFP facility of CHARMM. A minimization procedure involving the steepest descent (100 steps) and conjugate gradient (1,000 steps) algorithms was applied to the initial configurations, and then the temperature was raised from 100 to 300 K with a 1-K temperature increase every 80 steps. Atomic velocities were scaled every 500 steps during 50 ps to reach a temperature of 300 K and the runs lasted for 4.5 ns. The first part of each simulation (500 ps) was considered as an equilibration phase and the analysis was performed only on the remaining part (4 ns), over the configurations saved every 0.2 ps. To investigate the dependence of the results on the silica force field, additional simulations in which silica was represented by the CHARMM parameters developed by Lopes et al.³² (referred to as the CHARMM force field) were performed following the same procedure as above.

Results and Discussion

Density Profiles

Figure 2 shows the water density in the (*X*, *Y*) plane, ρ_{XY} , averaged in the *Z* direction over the length of the pore. The high-density spots found in the vicinity of the pore surface reveal a significant localization of water molecules due to the strong interaction with the pore and/or from the entrapment of water inside small surface cavities. Such a localization is not caused by a particular water–silica bonding pattern, but rather by the local geometry of the pore, which (1) favors close interactions of water with the pore surface and (2) does not allow an easy exchange of the entrapped water with the few surrounding water molecules, leading to long residence times. In the PH pore, two layers of homogeneously distributed spots can be identified; the distribution of spots in the two layers is more heterogeneous in the PL pore due to the higher rugosity of its surface. Surprisingly, regions of high density (>3 g/cm³) prevail more in the PL pore than in the PH pore. In the inner part of the pores, the water density fluctuates only slightly around the bulk value, and the water may thus be expected to behave similarly to bulk water in this region.

The radial density profiles $\rho(r)$ of both water molecules and silica shown in Figure 3 reflect the surface roughness of the pores. Some silica atoms belonging to the silanol groups are found at a radius *r* as low as 14 Å, whereas the average silica density ($\rho=2.2$ g/cm³) is reached only at *r*~17–18 Å. The PL surface is shifted by about 1 Å to larger *r* values compared with the PH surface due to surface relaxation.³³ The density profiles show a small shoulder around *r*=14 Å which is the consequence of the Si–OH addition in the surface reconstruction.³³

The density profiles of confined water are characterized by two main peaks close to the pore surface; their maxima at ~1.1–1.3 g cm⁻³ are not as large as those obtained locally in the two layers in Figure 2 (3–4 g cm⁻³), due to the radial averaging and smearing caused by the surface roughness. These peaks reflect the strong interaction of water molecules with the silica surface, as found in previous simulations,^{34–37} and recently confirmed by the experimental results based on neutron scattering experiments.^{38,39} Such a layering effect is expected to depend strongly on parameters such as the ratio between the size of the confined molecules and the pore diameter, the solvent–pore interaction strength, etc. The peaks are actually lower in the PL pore than in the PH due to the more heterogeneous surface and the greater roughness of the former. Finally, the water density converges to the bulk value in the central part of the pore in both types of pore, in contrast with values around 0.9 g cm⁻³ found in several previous simulations.^{34–36} This difference probably stems from the filling

procedure employed here,³³ which appears more realistic, as reported by Mancinelli et al.³⁸ A few water molecules are also located at $r > 17\text{\AA}$, penetrating small cavities of the silica matrix. The water density profiles in Figure 3 show clearly that the number of water layers structurally impacted by the interactions with the silica pore decreases steadily with the lowering of the silanol surface concentration. Then, the number of impacted layers should converge to one at the zero concentration limit.

Interfacial Water–Pore Interaction Energies

Interfacial water molecules are defined as water molecules whose oxygen atoms were within 4.5 or 5.5 $\text{\AA}$ from any O or Si atom of the substrate, respectively. Due to their differing topologies, the filling procedure led to different total numbers of confined water, $N_{\text{PH}}=1,396$ and $N_{\text{PL}}=1,647$, and as a consequence, different numbers of interfacial water molecules, $I_{\text{PH}}=556$ and $I_{\text{PL}}=603$. The high densities of water molecules observed at the surface of the silica pores indicate that interfacial water molecules are interacting strongly with the silica. The strength of these interactions was analyzed quantitatively from the average interaction energies. The total interaction energy between the interfacial water and the silica pore was found equal to -2.2 and -2.8 kcal/mol for the PH and PL pores, respectively. The vdW energy for PH (PL) represents -1.00 ± 0.03 kcal/mol (-0.90 ± 0.03 kcal/mol), and the electrostatic energy -1.20 ± 0.08 kcal/mol (-1.90 ± 0.08 kcal/mol). The total interaction energies are slightly smaller in absolute value than those between two hydrogen-bonded water molecules (approximately -5 kcal/mol); however, the distributions are broad, and some of the interactions are very strong. For instance, in the PH and PL pores, 1% and 5% of interfacial water molecules, respectively have interaction energies with silica higher in absolute value than 7.5 kcal/mol. Such large interaction energies were observed in confined methanol⁴⁰ with a broad distribution extending beyond 10 kcal/mol. The absolute value of the interaction energy increases with decreasing silanol concentration due to the enhanced electrostatic interactions; the absence of vdW parameters for silicon atoms favors close contacts between silicon and water molecules. An obvious conclusion is that an improvement of the description of water–pore interactions in the Brodka silica force field is needed.

Hydrogen Bond Network

Figure 4 shows the average number of hydrogen bonds (HBs) that a water molecule forms with other water molecules or with the silica surface. This number is almost constant at the value of 4 (as in bulk water) up to $r=14\text{\AA}$, after which it steadily decreases to 2.2–3.2 at $r=19\text{\AA}$, depending on the pore type. This decrease arises from (1) the partial substitution of water–water HBs by water–silica HBs and (2) the distortion of the water HBN near the pore surface. The water–pore and water–water HBs curves are shifted to higher r and change more smoothly in the PL pore because of its slightly larger diameter and surface roughness. The decrease of the total number of HBs implies that the interaction of water with silica does not perfectly balance the water–water interactions, in agreement with the average interaction energies discussed in the previous section. Interestingly, the magnitude of the decrease at $r \approx 17\text{--}18\text{\AA}$ correlates with that of the interaction energies between interfacial water and silica: the weaker the water–pore interaction strength, the stronger the induced decrease of total HBs per water.

The average number of water–silica HBs is given in Table 1. The total number of water–pore HBs does not change with the silanol surface concentration. In going from the PH to the PL pores, a decrease of the number of water–silanol HBs is observed, which does not scale with the silanol surface concentration. This behavior could be due to several factors including (1) the low solvent accessibility of some silanol groups, (2) the sharing of water

molecules between geminal silanols, (3) the larger number of silanol–silanol HBs in the PH pore, and (4) the different surface roughness of the two pores.

Tetrahedral Order Parameter

The orientational order parameter⁴¹ q was computed to quantify the deviation of the arrangement of a given water molecule and its four nearest neighbors from a perfect tetrahedral network. This order parameter is defined as follows:

$$q = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos(\Psi_{j,k}) + \frac{1}{3} \right)^2 \quad (1)$$

where $\Psi_{j,k}$ denotes the angle formed by the lines joining the oxygen atom of a given water molecule to those of the j th and k th nearest neighbors. For a perfect tetrahedral organization of water molecules, $q=1$, while for a random arrangement with uncorrelated uniform angular distribution, $q=0$. The O atoms of silica were allowed to be the nearest neighbors in the computation of q . The q distributions of water in the different radial regions of the PL pore are shown in Figure 5a. All distributions have a bimodal shape; the high- q peak may be ascribed to structured or ice-like water molecules, whereas the low- q peak is due to less structured or liquid-like water. The three distributions in the inner part of the pore ($r < 12\text{\AA}$) superimpose almost perfectly on each other and are very similar to the q distribution of SPC/E bulk water.⁴¹ In contrast, the distribution in the contact layer ($r > 12\text{\AA}$) is significantly shifted to lower q values and the amplitude of the low- q peak is higher than that of the high- q one. This suggests that the location of O atoms of the silica matrix prevents interfacial water molecules from forming a regular tetrahedral organization.

The orientational order parameter averaged over all water molecules $\langle q \rangle$ shown in Figure 5b is almost constant up to $r=12$ and $13\text{\AA}$ in the PH and PL pores, respectively, and steeply decreases for larger radii, showing that the organization of H₂O molecules at the pore surface is significantly modified by the presence of the silica wall. In contrast, the local organization of water molecules at the water/pore interface depends on the pore surface, in agreement with the water–pore HBs of Figure 4. The smaller $\langle q \rangle$ of the surface water in the PH pore may be ascribed to the larger number of silica hydroxyl oxygens that are first neighbors of water molecules. Local concentrations of silica OH groups can be rather high, particularly in the vicinity of the “triplet” patterns for which three OH groups are very close to each other within $3\text{\AA}$. Consequently, a water molecule with at least one OH group of such a pattern as nearest neighbor is likely to have another nearest neighbor from the same pattern. Since the second peak of the O–O radial distribution function of bulk SPC/E water is located around $r=4.5\text{\AA}$,⁴² a water molecule having two nearest neighbors from a triplet pattern is likely to have a distorted tetrahedral organization.

Translational Diffusion Coefficients

The translational diffusion coefficient of the water molecules D can be computed by fitting their mean square displacement (MSD) with the Einstein relation:

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{2dt} \quad (2)$$

where $\mathbf{r}(t)$ is the position vector of the center of mass of molecules at an instant t , the brackets represent averaging over every time origin and molecule, and d is the dimensionality of the diffusion. Given that the cylindrical shape of the pores prevents molecules from diffusing over long distances in the X and Y directions, only the mean

square displacement along the Z axis (MSD_Z) was considered with $d=1$. Previous studies have shown that the diffusion coefficient strongly depends on the distance of the molecules from the pore surface,^{34,35,43} so we accordingly considered different regions of the pores. To take into account the continual exchange between adjacent regions, which makes the set of molecules populating each zone time dependent, we decomposed the molecular dynamics (MD) trajectory of each molecule into time intervals where it stayed continuously in the region of interest except for very brief excursions of duration less than 1 ps. The MSD of molecules along the Z axis of the pore is then given by:

$$\text{MSD}_Z(t) = \frac{1}{\sum_{i=1}^N \sum_{j=1}^{n(i)} \tau_{\max}(i, j)} \times \sum_{i=1}^N \sum_{j=1}^{n(i)} \sum_{\tau=1}^{\tau_{\max}(i, j)} (z_{i,j}(t+\tau) - z_{i,j}(\tau))^2 \quad (3)$$

where $z_{i,j}$ is the position along the Z axis of the center of mass of a molecule i in the time interval j , N is the total number of molecules that belongs to the studied region, $n(i)$ is the number of time intervals of the molecule i which are equal to or larger than t , so that the molecule i can contribute to the computation of MSD at time t , and $\tau_{\max}(i, j)$ denotes the maximum number of time origins used in the computation of MSD for the j th time interval of the molecule i .

The MSD_Z values averaged over all confined water molecules are shown in Figure 6a. The corresponding translational water diffusion coefficients of water D_Z are equal to $2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in the core region for both pores and $2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the whole confined water for the PH and the PL pores, respectively. The significant decrease of the global diffusion coefficient of confined water with respect to bulk SPC/E water (~ 2.5 – $2.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at RT)^{30,44,45} may arise from: (1) the roughness of the pore surface and in particular the presence of small cavities, in which some water molecules are temporarily trapped and (2) the strong interactions of interfacial water with silica. Takahara et al.⁴⁶ studied the dynamical behavior of water molecules confined in MCM-41 mesopores ($\varnothing=28.4 \text{ \AA}$) by quasielastic neutron scattering experiments. They derived diffusion coefficients of water in the range 1.3 – $1.8 \times 10^{-5} \text{ cm}^2/\text{s}$, depending on the fitting method, in reasonable agreement with our results with slightly larger pore diameters ($\varnothing \approx 30$ and $32 \text{ \AA}$ for the PH and PL pores, respectively). Moreover, Spohr et al.³⁵ reported a significant decrease of the water diffusion coefficient in a cylindrical pore ($\varnothing=40 \text{ \AA}$) that scaled with the hydration level of the pore; their calculated value at full hydration ($1.8 \times 10^{-5} \text{ cm}^2/\text{s}$) is in agreement with our results for the PL pore. The comparison of experimental and computed diffusion coefficients suggests that the PL pore provides a better description of the experimental MCM-41 pores, as expected from the silanol surface concentration that compares well with experimental values (see Figure 1).

The MSD of water molecules were then computed in three different regions of the pore. The first region is composed of water molecules close to the pore surface ($r > 12$ or $13 \text{ \AA}$ for the PH and PL pores, respectively), which interact strongly with the pore surface via HBs, and whose motions are likely to be hindered by the surface rugosity. The remaining part of the PH and PL pores ($r \leq 12$ or $13 \text{ \AA}$) was decomposed into two domains of equal volume, a core region defined by $r \leq 8.5 \text{ \AA}$ or $9.2 \text{ \AA}$, and an intermediate region with $8.5 < r \leq 12 \text{ \AA}$ or $9.2 < r \leq 13 \text{ \AA}$, for the PH and PL regions, respectively. The resulting MSDs are shown in Figure 6b–d. The diffusion of water molecules near the silica surface is strongly subdiffusive because of the strong interfacial water–pore interactions. A similar non-Fickian behavior was reported for water molecules bound to the surface of a silica pore^{34,47} and at the surface of proteins,⁴ and was ascribed (1) to their roughness and (2) to the power law dependence of water residence times, which arises from the heterogeneity of water–surface

interactions. The MSD of water molecules in the intermediate region is almost linear, since some water molecules in this region may be slowed down by forming HBs with bound water molecules while it is linear in the core region. Moreover, significant differences between the MSD_Z of water confined in the two pores are essentially observed for interfacial molecules; they are smaller in the PL pore, owing to the stronger water–pore interaction energies (−2.8 and −2.2 kcal/mol for the PL and PH pores, respectively). Besides, the values of D_Z in the core region are in line with those of the bulk SPC/E water at RT ($\sim 2.5\text{--}2.8 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$)^{30,44,45} and in fair agreement with the experimental values ($2.2\text{--}2.3 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$).^{48,49} Therefore, it may be inferred that water molecules behave essentially like bulk water in the core region. It must be pointed out that Spohr et al.³² obtained a larger diffusion coefficient, $3.1 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, in the $r = 6 \text{ \AA}$ region of their simulated pore ($\phi = 40 \text{ \AA}$) at full hydration, with a corresponding water density of about 0.9 g cm^{-3} . The comparison with the present results indicates that the filling procedure is a crucial step in the simulation of confined liquids when performed in the microcanonical and canonical ensembles, since a slight error in the number of confined molecules, by only a few percent, is likely to change the structural and dynamical behavior of confined molecules in the inner part of the pore. Spohr³⁵ estimated that about 100–150 more water molecules, out of 2,600, would be needed to reach bulk water density in the central part of their pore. The filling procedure used in the present study³³ seems to give satisfying results, since the structural and dynamical properties of water molecules from the core part of the different pores are similar to those of bulk water.

Influence of the Silica Force Field

To investigate the impact of the silica force field on the properties of water, we used the recent CHARMM silica force field³² initially developed to represent crystalline quartz–water interactions. A slightly larger number of H_2O molecules were confined during the filling procedure (1,682 vs. 1,647) and the water localization was also found to be slightly stronger. These differences can be ascribed to (1) the absence of vdW parameters for Si atoms in the Brodka force field³¹ and (2) the larger dipole moment of the O–H bond in the CHARMM force field. Consistently, the interfacial water–pore interaction energies are stronger with the CHARMM force field by about 1 kcal/mol (−3.8 kcal/mol vs. −2.8 kcal/mol). The $\langle q \rangle$ of interfacial water molecules was also higher with the CHARMM force field because the slightly enhanced local water density obtained with this force field increases the probability for a given surface water molecule to have another water molecule as a neighbor. Finally, the MSD and D_Z of water were systematically found slightly smaller with the CHARMM force field (2.6 and $1.7 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ vs. 2.7 and $1.8 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, when averaged over all water molecules or over only *core* water, respectively), given the larger interaction strength of water with the silica walls. Overall, the structural and dynamical properties of water molecules confined in the PL pore were found quite similar with the two force fields, suggesting that this pore reproduces satisfactorily the confining effects of the MCM-41 pores used experimentally to study confined water.

Conclusions

The main goal of the present study was to investigate the influence of the silanol surface concentration on the structural and dynamical properties of water confined in cylindrical pores that mimic MCM-41 mesopores. The procedures employed in the present study to construct the model pores in the silica matrix give a more realistic distribution of hydroxyl groups on the surface, as compared to the experiment, than previously used methods. Because of the importance of surface topology in determining interactions with water confined in pores, a reasonable surface hydroxyl density is essential for developing a useful description of confined water structure and dynamics. With the present procedures, water

molecules were observed to strongly hydrate specific locations on the surface in response to the curvature and local hydrogen bonding environment, which produces, as might be expected, a layer of water with orientational and hydrogen bonding profiles that differs from bulk water, with corresponding effects on dynamical behavior. For both the PH and PL pores a strong interaction of water molecules with specific sites of the pore surfaces was observed. The resulting gradients in both dynamical and structural properties are in general qualitative accord with expectations. The translational diffusion coefficient of water determined experimentally in MCM-41 pores of similar diameters⁴⁶ was more satisfactorily reproduced in the PL pore than in the PH pore. This suggests that this pore provides a reasonable model of MCM-41 mesopores, since the silanol surface concentration compares well with the experiment.

The effects of the silica force field used are rather small. Water-silica interactions were found to be slightly stronger when silica was represented by the CHARMM potential,³² which essentially results in a slightly higher water localization and a slowing down of interfacial water molecules. Due to the importance of surface interactions, realistic non-bonded parameters for silica are required, as shown by Cruz-Chu et al.,⁵⁰ who developed a set of parameters compatible with the CHARMM force field that takes into account the shape of glassy silica (planar surface, cylindrical pore, etc.). For force field validation, a systematic comparison with the experimental data, in particular with those from neutron diffraction experiments, would be required, and is beyond the scope of this work. Nevertheless, the new results reported here demonstrate that the simulations performed with the PL pore describe relatively well the behavior of water confined in hydrophilic cylindrical pores. Therefore, this pore can be used in subsequent MD investigations of confined aqueous glucose solutions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Variation of the number of surface silanol groups in MCM-41 materials with heat-treatment temperature from NMR, adsorption, and thermogravimetric measurements. The values for conventional amorphous silica are given as a rough guide

Fig. 2. Average local XY densities ρ_{XY} of water in the PH and PL pores. The density scale is 0–4 g/cm³

Fig. 3. Water density profiles $\rho(r)$ in the PH and in the PL pores as a function of distance from the pore axis. The density profile of the silica matrix is also shown to locate the pore surface (*partial* and *plain gray shadings* for the PH and PL cases, respectively)

Fig. 4. Mean number of HBs that a water molecule forms with another water molecule or with the silica pore as a function of distance from the pore *Z* axis. An HB between O atoms was considered to exist if the O–O distance is $<3.4\text{\AA}$ and if the O–H–O angle is $>120^\circ$. The density profile of the silica matrix for the PH and PL pores (*partial* and *plain gray shadings*, respectively) is shown to locate the pore surfaces (the density scale is identical to that in Figure 3)

Fig. 5.
a Distribution functions of q of water molecules in different radial regions of the PL pore. **b** Radial evolution of $\langle q \rangle$ for the PH and PL pores. The density profiles of the silica matrix for the PH and PL pores (*partial* and *plain gray shadings*, respectively) are shown in order to locate the pore surfaces (the density scale is identical to that in Figure 3)

Fig. 6.

Mean square displacement along the Z axis (MSD_Z) of the center of mass of water molecules **a** in the whole pores or in distinct parts of the pores, **b** at the surface ($r > 12\text{\AA}$ or $r > 13\text{\AA}$), **c** in the intermediate region ($8.5 < r < 12\text{\AA}$ or $9.2 < r < 13\text{\AA}$), and **d** in the core region ($r < 8.5\text{\AA}$ or $r < 9.2\text{\AA}$). The additional *gray lines* with a unity slope are plotted to qualitatively estimate if the linear diffusion regime is reached

Table 1

Statistics of water-pore HBs

Pore type	HB type		
	Water-silica matrix	Water-silanol	Total
PH	23 (4)	307 (14)	330 (14)
PL	129 (8)	193 (10)	322 (13)

Standard deviations from mean values are indicated in parentheses