



Water in porous glasses. A computer simulation Study

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We report molecular dynamics simulations of water confined in a cylindrical silica pore. The pore geometry and size is similar to that of typical pores in porous Vycor glass. In the present study we focus on the dependence of microscopical structural and dynamical properties on the degree of hydration of the pore. We have performed five simulations of systems between 19 and 96 % hydration. In all cases, water adsorbs strongly on the pore surface, clearly demonstrating the hydrophilic nature of the Vycor surface. Two layers of water molecules are affected strongly by the interactions with the glass surface. With decreasing degree of hydration an increasing volume in the center of the pore is devoid of water molecules. At 96 % hydration the center is a continuous and homogeneous region that has, however, a lower density than bulk water at ambient conditions. A well-pronounced mobility profile exists, where molecules in the center of the pores have substantially higher self diffusion coefficients than molecules on the pore surface. The spectral densities of center of mass and hydrogen atom motion show the signature of confinement for the molecules close to the pore surface, while the spectral densities in the center of the pore are similar to those in bulk water. The molecular dynamics results are in good agreement with recent experiments. Our data indicate that the dependence of experimental data on the level of hydration of the Vycor sample is due to the different relative contribution of molecules adsorbed on the pore surface and bulk-like molecules in the interior of the pore to the experimental averages.

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1 Introduction

In recent years substantial experimental effort was dedicated to the elucidation of the microscopic structural and dynamical properties of water near interfaces and of 'confined' water. Confined water can be found in many environments, in porous media such as rock or sand stone, in the interior of living cells, or bound at the surface of synthetic macromolecules, biopolymers and membranes, or in a wide variety of gel-forming substances. One of the driving forces to undertake basic research on such complicated systems is the assessment of how the hydrogen bond network in water reacts to vastly different perturbations and how in turn the properties of the network determine the catalytic and dynamic properties of these systems. Porous Vycor glass is one of the most interesting materials with relevance to catalytic and separation processes and has recently been studied extensively by various experimental techniques. [1–16]

Computer simulations are ideally suited to investigate some aspects of the microscopic properties of such complex systems, if one keeps in mind, however, the limitations due to an incomplete knowledge of intermolecular interactions and the limits on system size and observation time imposed by the finiteness of computational resources. Nevertheless, a multitude of simulation studies has been performed, many of which are reviewed, e. g., in Refs. [17–23]. Recently, one of us (MR) and his coworkers [24,25] performed Molecular Dynamics (MD) simulations of a water-filled pore of 40 Å in diameter inside a block of Vycor glass. In that first study, the pore was almost completely filled with water molecules and the total simulation time was very short. In the present study, we investigate five systems with different amounts of water inside the pore ranging from approximately 19 % to 96 % of hydration. The simulations have been carried out for sufficiently long times so that dynamic properties like the self diffusion coefficient can be determined reliably both as a function of water concentration and as a function of position within the pore.

In the following section we will briefly summarize the simulation technique used, which is standard molecular dynamics. Then we will discuss the structure inside the pore by means of profiles of atom densities, coordination number and number of hydrogen bonds. The dynamic properties are described by position-dependent self diffusion coefficients and mean square displacements and by the spectral densities of translational and rotational motion. In a final discussion we will relate our simulation results to the relevant experiments.

2 Molecular Dynamics Simulations

We have modeled a cylindrical cavity in a porous glass such as Corning Vycor glass [26] by following the method proposed by Brodka and Zerda[27]. In short, a cylindrical cavity of 40 Å of diameter has been cut out from a previously simulated configuration of vitreous silica by first eliminating all atoms lying within a distance $R = 20$ Å from the z -axis, then eliminating all silicon atoms with less than four oxygen neighbours, and finally saturating the valence of those oxygen atoms with only one silicon neighbour (termed nonbridging oxygens) with hydrogen atoms. The preparation of the pore is explained in detail in Ref. [24]. The procedure results in a cavity with corrugated surface and roughly cylindrical shape. The final block of material is a cube of length $L = 71.2903$ Å containing a total of 6382 silicon atoms, 227 acidic hydrogen atoms, 227 nonbridging and 12478 bridging oxygen atoms. The number of acidic hydrogen

Table 1

Summary of simulation parameters. N_W is the number of water molecules, T the temperature in K, t the simulation time used for data analysis and t_{eq} the equilibration time.

N_W	% hydration ^(a)	T/K	t /ps	t_{eq} /ps
500	19	298.3	240	340
1000	38	298.3	740	320
1500	58	298.4	300	180
2000	77	298.4	360	110
2600	96	298.7	90	50

^(a): based on estimated value for full hydration $N_W \sim 2700$ molecules (see text)

atoms corresponds to a surface density of about 2.5 nm^{-2} , in good agreement with the value of 2.3 nm^{-2} determined experimentally in Ref. [9].

Water is described by the SPC/E model [28]. Water molecules interact with the substrate atoms using the empirical potential model by Brodka and Zerda[27], which consists of (12-6) Lennard-Jones and Coulomb interactions. The potential parameters are identical to those used and tabulated in Ref. [24].

In the present study we have simulated samples of 500, 1000, 1500, 2000, and 2600 water molecules at room temperature, which are free to move within the cylindrical pore in the Vycor block. These runs correspond to hydration between 19 and 96 % of the maximum possible value. Further simulation parameters and some averages are summarized in table 1. All atoms in the Vycor block are immobile. They produce a static, although complex, external potential that acts on the water molecules.

All runs were started from either a distorted cubic lattice or from a random distribution of water molecules inside the cavity and were equilibrated for 50 or more picoseconds. Data sampling continued for times between 90 picoseconds and 1 nanosecond. The SHAKE algorithm [29] was employed to integrate the equations of motion. Temperature was controlled to room temperature by coupling the water degrees of freedom to a Berendsen thermostat [30] with time constant of 0.5 ps.

We used the shifted force method to smoothly truncate all interactions, including the Coulomb interactions at 9 \AA . The more rigorous treatment of the Coulomb interaction by, e. g., the Ewald summation method, was considered unfeasible, since the rather long simulations reported here are already very time-consuming with the much faster shifted-force scheme. Using Ewald summation would increase computation times by almost an order of magnitude. We did check, however, the influence of the truncation of the Coulomb interactions by a simulation of 2600 water with twice the usual cutoff, i. e., 18 \AA , and did not find substantial differences in the properties reported below. We also made a very short (5 ps) run using full Ewald summation, for which we analysed the static properties, and did again not see differences which would in-

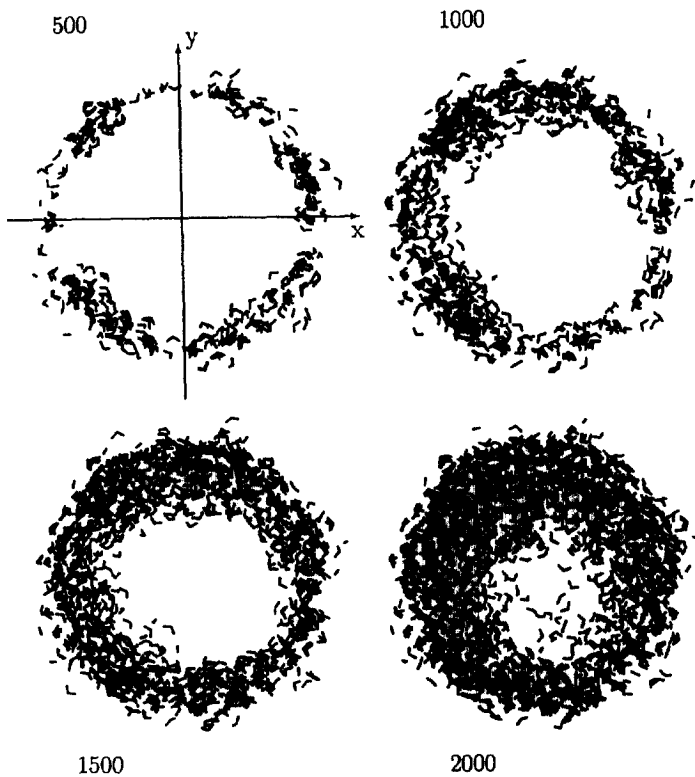


Fig. 1. Snapshots from simulations of pure SPC/E water inside a cylindrical cavity of radius 20 Å. Only water molecules are shown.

validate the conclusions drawn below, which are anyway based more on trends than on absolute numbers.

3 Results

3.1 Density Distributions

Figure 1 shows snapshots from 4 simulations. Only water molecules are displayed. The hydrophilic nature of the Vycor block is evident, since all water molecules are attracted towards the pore surface. With increasing level of hydration, the center of the cylindrical cavity is increasingly filled with water molecules. The distribution of water molecules is not very homogeneous. The 'cavity' in the water structure is usually not centered around the origin of the coordinate system. From the set of simulations shown here there is no indication for a water 'droplet' in the center of the pore as was observed in Ref. [24]. In Ref. [24], the simulation time was probably too short to obtain an equilibrium distribution of water molecules within the pore.

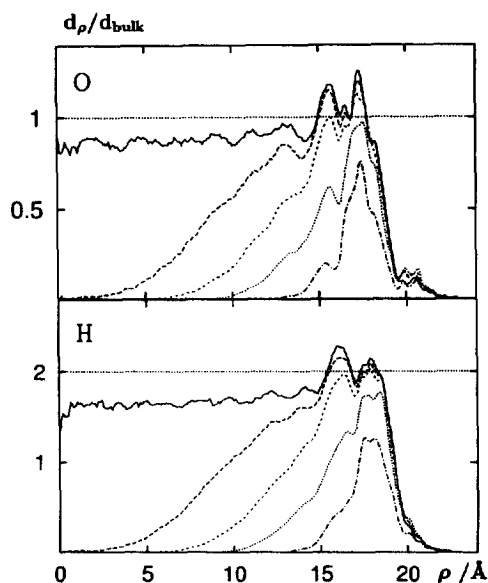


Fig. 2. Radial density profiles (normalized to the bulk density of water at ambient condition) of oxygen atoms (top) and hydrogen atoms (bottom) from all five simulations summarized in Table 1: $N_W = 2600$ (full), $N_W = 2000$ (long dashes), $N_W = 1500$ (short dashes), $N_W = 1000$ (dotted), $N_W = 500$ (dashdotted).

The asymmetry of the hole is possibly connected to the very slow approach to equilibrium and the long simulation times necessary before converged observables are obtained. Due to the use of the Berendsen thermostat the sample temperature is roughly constant but initially a long-time drift to lower total energies is observed which requires the long equilibration times. Successive snapshots, similar to Fig. 1, tend to look more centrosymmetric. The mass exchange either through the empty space in the center or along the inner surface of the water film is apparently quite slow.

Figure 2 shows the radial density profiles, d_ρ , of oxygen atoms (top) and hydrogen atoms (bottom) as a function of the distance ρ from the pore axis, normalized to the density of bulk water, d_{bulk} , at room temperature. Even at low levels of hydration ($N_W = 500$) the distribution is rather wide, and both density profiles already show indications of a second layer. No molecules are found in the pore center. With increasing filling of the pore, a first layer (around $\rho = 18 \text{ \AA}$) builds up, which becomes saturated around 58 % hydration. Simultaneously, the tail of the density distribution grows towards the center. The second layer (around $\rho = 16 \text{ \AA}$) saturates around 77 % hydration, corresponding to 2000 water molecules. Only at the highest level of hydration which we studied, with 2600 water molecules, we observe a continuous aqueous phase without a cavity in the center of the pore. The density in the center of the pore is about 0.9 g cm^{-3} in this particular run.

Since the density of the 2600 water run is rather constant in the range $0 < \rho < 14 \text{ \AA}$ (with a slight decrease towards the center) and does not show any indication of substrate-induced oscillations, we expect this region to be more or less bulk-like at full hydration. Assuming that the final density will be equal to the density of bulk water at ambient conditions, we estimate that about 100 to 150 more molecules are needed to fully hydrate this particular pore. A more rigorous way to determine the maximum filling of this particular pore is by means of grand canonical simulations, which we plan to undertake in the near future.

At all levels of hydration there is a small amount of molecules in the range $\rho > 19 \text{ \AA}$. These molecules are located in small 'pockets' near the surface of the large cylindrical pore. The pockets are produced as a consequence of the construction of the pore and are a manifestation of the rough nature of the pore surface. The water molecules also show up as isolated molecules outside the main ring of water molecules in Fig. 1. Detailed analysis shows that they are extremely immobile and, in many cases, do not move (apart from trivial oscillations in their 'cage') during the entire simulation (see also below).

3.2 Cluster Formation

Agamalian *et al.* [10] concluded from their neutron diffraction study that both compact water clusters of between 40 and 60 water molecules and individual molecules or small groups of molecules exist on the surface of Vycor glass. While it is clear from the density profiles in Fig. 2 and from the analysis of hydrogen bonds (see below) that the hydrophilic Vycor surface supports a continuous hydrogen bond network at high levels of hydration, 500 water molecules are insufficient to completely hydrate the glass surface. Figure 3 shows a snapshot of the water molecules and the acidic hydrogen atoms on the Vycor surface (taken from the simulation with $N_W = 500$). Here, the cartesian coordinates (x, y, z) of water molecules and hydrogen atoms are transformed to cylinder coordinates $(\rho, \rho_0, \varphi, z)$. $\rho = \sqrt{x^2 + y^2}$ and $\varphi = \arctan(y/x)$ are the usual cylinder coordinates and ρ_0 is a scaling factor, which brings the scale in the φ direction into rough agreement with that of the z direction, and has been chosen as the position of the maximum water density in Fig. 2 ($\rho_0 = 17 \text{ \AA}$).

The snapshot shows a wide distribution of cluster sizes, from isolated molecules to a rather large patch of water molecules (top, left of center) which contains approximately 100 molecules. Cluster composition and location change slowly with time. Interestingly, and perhaps contrary to expectation, many of the acidic hydrogen atoms on the Vycor surface do *not* engage in hydrogen bonds with water molecules. Troughs between patches of acidic hydrogen atoms seem to be hydrated preferentially. Note, e. g., some horizontal troughs on the left and a vertical trough near the right edge of the figure; the latter reaches through the entire pore. Apparently, water molecules prefer the formation of hydrogen bonds with the bridging oxygen atoms (see discussion below).

3.3 Hydrogen Bonding

We have analyzed the number of neighbours and the number of hydrogen bonds in which a molecule engages as a function of the radial coordinate ρ . Two water molecules are termed

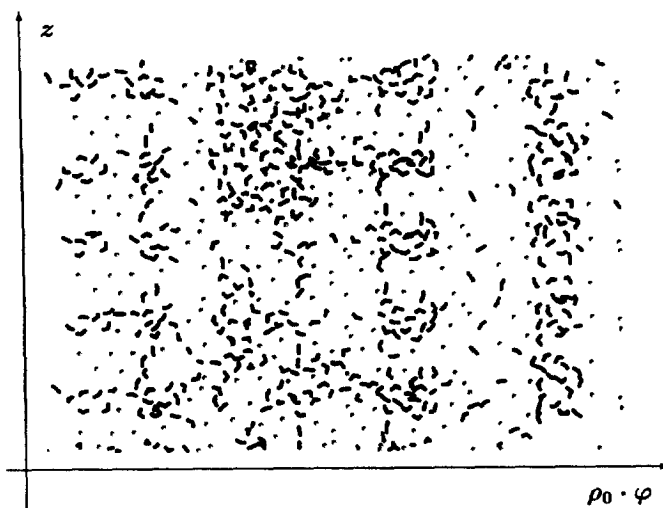


Fig. 3. Snapshot from a configuration of the $N_w = 500$ simulation. In this distorted representation the cylinder mantle has been cut open at $\varphi = \pi$. The abscissa contains the quantity $\rho_0 \cdot \varphi$, with the cylinder coordinate φ and $\rho_0 = 17 \text{ \AA}$ the average position of the molecules. It is parallel to the circumference of the cylinder. Water molecules are displayed by black lines and the acidic hydrogen atoms of the Vycor block are represented by grey spheres.

neighbours if the oxygen-oxygen distance is smaller than 3.35 \AA . They are termed hydrogen bonded if, in addition, the angle between an intramolecular O-H vector and the intermolecular O-O vector is smaller than 20° . Figure 4 shows the average number of neighbours, figure 5 the average number of hydrogen bonded neighbours per molecule. Each bond is counted only once. Figure 5 contains additionally the number of hydrogen bonds formed between hydrogen atoms of water molecules and bridging oxygen atoms the Vycor surface (long dashes) and the sum of the two contributions (short dashes). The number of hydrogen bonds between water molecules and the acidic H atoms of the Vycor surface is so small that it would leave the total number of hydrogen bonds almost unchanged on this scale. The relatively larger importance of those hydrogen bonds where the atoms on the Vycor surface are acceptors is consistent with the above-mentioned fact that, at low water concentration, cluster formation seems to start preferentially in regions with only few acidic hydrogen atoms (Fig. 3).

The number of neighbours and the number of water-water hydrogen bonds increase from the pore surface towards $\rho \approx 17 \text{ \AA}$. At low levels of hydration the maximum values are lower than at higher levels due to the fact that an insufficient number of molecules is available for hydrogen bond formation. The number of neighbours decreases towards the center of the pore, even at the highest levels of filling. The number of hydrogen bonds, on the other hand, is approximately constant over the entire central region of the pore at high levels of hydration and decreases more slowly in the center at intermediate levels of hydration. Even if the number of neighbours (and consequently the local density) is reduced, the number of hydrogen bonds can be very high. The

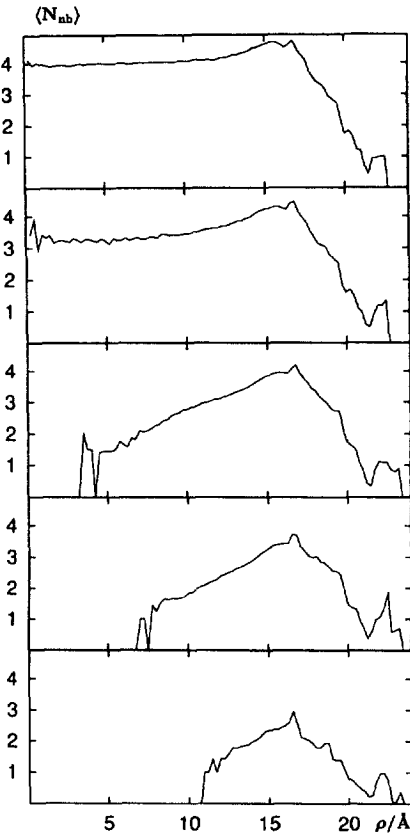


Fig. 4. Average number of neighbours as a function of ρ in five simulations at different levels of hydration in a Vycor pore.

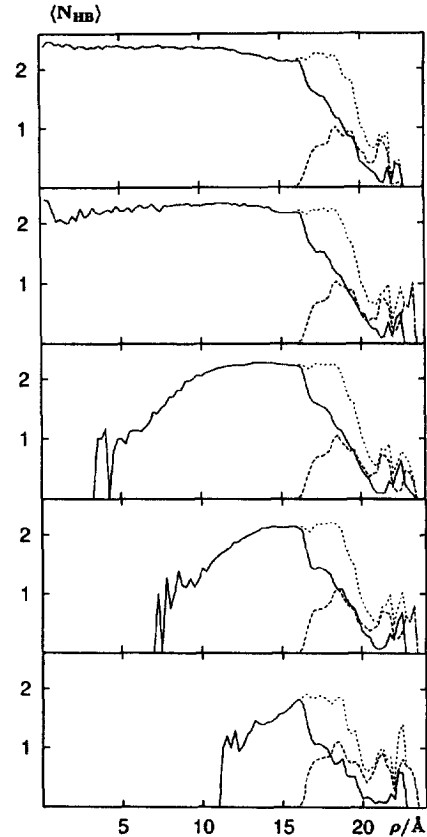


Fig. 5. Average number of hydrogen bonds (for definition see text) as a function of ρ in five simulations at different levels of hydration in a Vycor pore. Full lines show the number of water-water bonds, long-dashed lines the number of bonds between water molecules and bridging oxygen atoms, and short-dashed lines denote the sum of the two.

phenomenon, that the actual water structure in an inhomogeneous environment is the result of the maximization of the number of hydrogen bonds under the geometrical constraints present, is quite general and has been observed in many simulations of water near planar hydrophobic, hydrophilic, and metallic surfaces as well as in cylindrical pores [31]. Figure 5 also shows that near the pore surface the number of hydrogen bonds between water and Vycor balances the loss of water water hydrogen bonds to a large extent. This again is a very clear indication of the hydrophilic nature of this surface.

Table 2

Self diffusion coefficients as calculated from the mean square displacement $\langle \Delta z^2 \rangle$ (in units of $10^{-5} \text{cm}^2 \text{s}^{-1}$) in the direction along the pore axis for the total aqueous phase and for various cylindrical shells as indicated. Statistical errors are of the order of $0.2 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$.

$N_{\text{H}_2\text{O}}$	0-6	6-10	10-14	14-16	16-18	18-22	total
500		1.0			0.2	0.0	0.3
1000		2.9		1.6	0.4	0.0	0.8
1500		2.9		1.5	0.4	0.0	1.2
2000	3.7		2.7	1.7	0.4	0.0	1.6
2600	3.1	2.8	2.6	1.5	0.4	0.0	1.8

3.4 Water Mobility

We have calculated the self diffusion coefficient (SDC) of water molecules along the pore axis from the mean square displacement in the z direction, Δz , according to

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta z^2 \rangle}{2t} \quad (1)$$

with t the time. The results are summarized in Table 2.

In addition to the total SDC (the average over all water molecules) we have separately calculated the SDC of water molecules located at $t = 0$ in various cylindrical rings. The total self diffusion coefficient is smaller than in bulk water (2.53 (Ref. [32]) and $2.59 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$ (Ref. [33]) for the SPC/E model) and increases with increasing level of hydration. From the remaining data

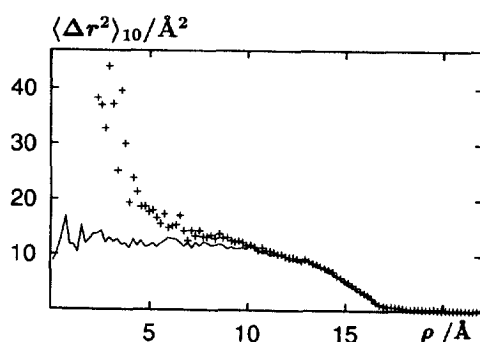


Fig. 6. Mean square displacement $\langle \Delta r^2 \rangle_{10}$ after 10 ps as a function of the initial distance ρ of a water molecule from the pore axis for the two runs with 2600 (full line) and 2000 (symbols) water molecules.

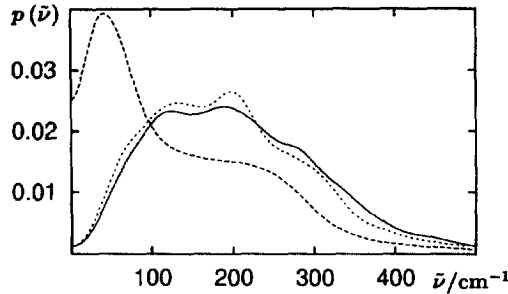


Fig. 7. Spectral density $p(\tilde{\nu})$ of the center of mass motion: $N_W = 2600$ and $\rho > 18 \text{ \AA}$ (full line), $N_W = 2600$ and $\rho < 6 \text{ \AA}$ (long dashes), $N_W = 1000$ and $\rho > 18 \text{ \AA}$ (short dashes).

in the table it is evident that there is a large gradient of the mobility between the region near the pore surface (lowest mobility) and the center of the pore (highest mobility), similar to the results we obtained in polar model pores [34]. The SDC in the various regions does not depend strongly on the degree of filling of the pore.

Figure 6 shows mobility profiles across the two pores with the largest water concentration. The figure displays the mean square displacement after 10 ps as a function of the ρ coordinate of the water molecule at initial time. The mobility is highest in the center of the pore and lowest near the pore surface. At very high water concentration (full line) the mobility is more or less constant in the range $0 < \rho < 10 \text{ \AA}$ and then decreases monotonically. Beyond about $\rho = 18 \text{ \AA}$ the mean square displacement is very small and the adsorbed water molecules in this range do not contribute to the total transport coefficient along the pore axis. If the pore is not completely filled and if there is an 'empty' region in the center (symbols) the mean square displacement is not constant in the inner region of the cylinder. The mobility keeps increasing towards the pore center, which is due to the fact that water molecules near a free surface are more mobile than in the interior of the liquid phase, since they are bonded to the liquid by a smaller than average number of hydrogen bonds (see Fig. 5). The behaviour near the Vycor surface at lower water concentration is unchanged from that at the highest concentration.

3.5 Spectral Density of Water Motion

Figure 7 shows the spectral density of the center of mass motion of water molecules, obtained from the Fourier transform of the center of mass velocity autocorrelation function (vacf) according to

$$p(\tilde{\nu}) = 2\pi c \int_0^{\infty} c_{vv}(t) \cos(2\pi c \tilde{\nu} t) dt \quad (2)$$

where t is the time, $c_{vv}(t)$ the vacf, and c the speed of light. The figure contains the spectral density of molecules in the range $\rho < 6 \text{ \AA}$ (long dashes) in the system with 96 % hydration and

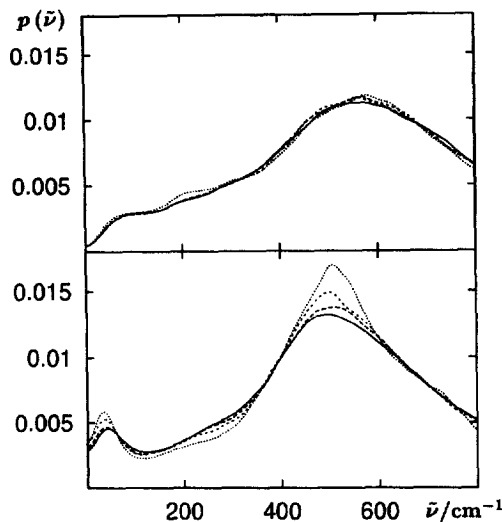


Fig. 8. Spectral densities $p(\tilde{\nu})$ of hydrogen atom translational motion for the adsorbate region $\rho > 16$ Å (top) and the pore center $\rho < 14$ Å (bottom) for four different simulations: $N_W = 2600$ (full), $N_W = 2000$ (long dashes), $N_W = 1500$ (short dashes), $N_W = 1000$ (dotted).

for $\rho > 18$ Å at 96% hydration (full line) and at 38 % hydration (short dashes). We first note that the spectral density in the center of the pore is similar to those found in the bulk phase [32]. Near the surface, the relative intensity of the two spectral features near 50 and near 200 cm^{-1} changes and the center of the distribution shifts to higher frequencies. The shape of the spectral density is characteristic for the confinement of water; a similar shape has been observed also near planar interfaces [35]. The low values of $p(\tilde{\nu})$ at $\tilde{\nu} = 0$ clearly show the drastic reduction of the self diffusion coefficient near the Vycor pore surface.

Figure 8 shows the spectral densities of the hydrogen atom motion. The top frame contains data for water molecules near the Vycor pore surface ($\rho \geq 16$ Å), the bottom frame the corresponding data for the center of the pore ($0 < \rho < 14$ Å). $p(\tilde{\nu})$ near the Vycor surface is independent of the level of hydration. The shape of the spectral density of molecules in the center of the pore is very similar to the corresponding function in bulk water; the small differences in the intensity of the translational maximum around 60 and the rotational maximum around 500 cm^{-1} mainly reflect the different average densities of the molecules in the center of the pore. The maximum around 60 cm^{-1} vanishes completely for those molecules near the Vycor surface. At the same time, the maximum of the rotational contribution to the spectral density increases from around 500 to almost 600 cm^{-1} . The results are in excellent agreement with the inelastic neutron scattering experiments by Bellissent-Funel et al. (Figure 8 in Ref. [14]).

4 Summary and Discussion

The structural properties of confined water in Vycor glass have been investigated in a series of scattering experiments. In earlier work Bellissent-Funel et al.[11] observed that the structure

factor of confined water is very similar to that of bulk water. More recently Soper, Ricci and coworkers [15,16] performed neutron diffraction experiments with isotopic substitution and concluded that water confined in porous Vycor glass is still hydrogen bonded, but that the bond network is strongly distorted. Bellissent-Funel, Chen and their coworkers [11–14] additionally studied, by inelastic neutron scattering, the single particle dynamics of water in the same material as a function of the level of hydration (i. e., the amount of water in the pore relative to the maximum observable amount). Motivated by these studies, we performed classical molecular dynamics computer simulation studies of water in a cylindrical model Vycor pore as a function of water content, using realistic potential functions for water-water and water-Vycor interactions.

The simulated Vycor pores are very hydrophilic in nature. Low amounts of water are almost completely adsorbed on the substrate surface, although some water molecules (hydrogen bonded to adsorbed molecules) are found in the second layer. A wide variety of water clusters is visible at low water concentration. The presence of such water clusters has been postulated previously by Agamalian et al. [10] on the basis of small-angle scattering and powder diffraction data. With increasing water concentration, water molecules occupy an increasing fraction of the free volume of the pore. Simultaneously, the amount of water in the adsorbed layer saturates at hydration levels $> 58\%$, that of a second layer at hydration levels $> 77\%$. The density maxima are not very pronounced, compared, e. g., with those observed in typical simulations of water near metallic surfaces. A continuous water phase (without a cavity of roughly cylindrical shape in the center) forms only at the highest levels of hydration ($> 80\%$).

Our MD results show a strong reduction of the water-water hydrogen bonds close to the pore surface, where the hydrogen bonds between water molecules and functional groups of the Vycor material balance to a certain extent the decrease of water-water hydrogen bonds. A more detailed analysis of the structural properties would be necessary in order to determine whether the tetrahedral ordering is perturbed by the interaction with the substrate, as indicated by recent experimental[15,16] and computer simulation[24,25] results.

There is some conflicting evidence from neutron diffraction and NMR spectroscopy concerning the dynamics, specifically the self diffusion coefficient, of water inside the pore. Short time diffusion coefficients (obtained from the line shape analysis of inelastic neutron scattering data) indicate an almost unchanged, possibly even higher, SDC of water in the fully hydrated pores and a reduction of the SDC with decreasing level of hydration (down to 25%), while NMR data who probe water dynamics on a much longer time scale indicate a more substantial reduction of water mobility. Our simulation data show, first of all, that there is a mobility profile across the pore. The mobility of molecules directly adsorbed on the surface is reduced by more than an order of magnitude. At the same time, the SDC of water molecules in the central part of the pore is roughly the same as the SDC of the SPC/E model in the bulk phase. Consequently, the total SDCs (see Table 2) are only slightly lower than in the bulk phase. The total SDC decreases with decreasing level of hydration. The neutron scattering experiments, which probe only the total water dynamics, show a similar trend with level of hydration.

The spectral densities of center of mass motion and of hydrogen atom motion show the signature of confinement which results in the shift of the maxima to higher frequencies and the

disappearance of low frequency features characteristic for the bulk phase. Our simulated hydrogen spectral densities are in excellent agreement with the neutron scattering results, with respect to actual peak positions, their shifts and relative intensities.

In summary, our simulation data are in good agreement with the available experimental evidence concerning the structure and single particle dynamics of water in Vycor pores. Therefore, we have some confidence that the interaction model used in our study captures at least some of the essential properties of the system. This, in turn, will enable us to investigate the properties of water confined in Vycor glass in more molecular detail than is currently available from experiments, which we plan to do in the near future.

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