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Water in confined geometries: experiments and simulations

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Abstract. This paper presents the state-of-the-art in studies of structure and dynamics of water confined in a prototype hydrophilic substrate: porous Vycor glass. Experimental data and molecular dynamics simulations are compared.

1. Introduction

The observation that in many relevant situations water is confined in different environments (typical examples are water in rocks, in sandstones, in biological cells, or at the surface of proteins and membranes) explains the increasing number of studies of the structural and dynamical properties of confined water in the recent literature [1].

From the experimental point of view it is important to find a confining substrate with well defined geometrical characteristics, that is easy to handle, and as transparent as possible to the experimental probe. In order to interpret the data it would be very useful to have the proper simulation to compare it with, while usually computer simulations are performed in extremely simplified model systems, such as two infinite parallel plates [2], since most real cases are not easy to simulate due to the complexity of the substrate at the molecular level. Porous Vycor glass matches most of the above requirements. It offers, to water, a well characterized hydrophilic network of cylindrical pores, is composed of simple molecules (SiO_2), and does not change its dimensions upon hydration. The typical dimension of the diameter of a pore is of the order of 4–5 nm, i.e. of the same order of magnitude as most biological confining environments. Last, but not least, a potential model for the Vycor–solute interaction is available in the literature [3]. For all the above-mentioned characteristics porous Vycor glass has been widely used as a substrate for studies of confined water [4–12]. Until recently, however, considerable discrepancies were present in the interpretation of results from different techniques or by different authors. As a matter of fact, in a pioneering neutron diffraction work, performed on D_2O , no sensible differences between room-temperature data and bulk water at ambient conditions were observed, while it was argued that the structure of the water layers closer to the interface appears to be markedly different from that of bulk water upon lowering the temperature [4]. Conversely in a recent neutron diffraction experiment, applying the isotropic H/D substitution, strong distortions of the hydrogen bond network compared to bulk water were detected at room temperature [5]. As far as the diffusional dynamics are concerned, nuclear magnetic resonance (NMR) studies have been interpreted in terms of the slowing down of the rotational dynamics compared to bulk water and longer residence times in the first hydration shell [6]. These findings partially contrast with the classical analysis of quasi-elastic neutron scattering experiments, leading to

values of the rotational diffusion coefficient in agreement with those found for bulk water [7], and with the residence time found in simulations of water close to hydrophilic surfaces [2]. Finally, it has to be mentioned that it has recently been argued from quasi-elastic neutron scattering experiments that confining water in small hydrophilic environments may be equivalent, at least as far as its translational dynamics is concerned, to supercooling bulk water [8] and that new high-resolution data have been shown to fit the lineshape predicted by the mode coupling theory for a fluid approaching its glass transition [9]. Most of the discrepancies exposed above are due to the complexity of the data analysis when a substrate and a solute are present.

The aim of this paper is to show how ‘ad hoc’ molecular dynamics (MD) simulations, performed in a system as realistic as possible, may support the interpretation and analysis of experimental data and stimulate new experimental studies. Such simulations have been recently performed for simple point charge/extended (SPC/E) water confined in a simplified model of Vycor glass [10, 11].

2. Microscopic structure

The details of the neutron diffraction experiment and of the MD simulations can be found in [5] and [10, 11], respectively.

As far as the experiment is concerned, we only want to stress here the contrasting aspects between [4] and [5]. First of all the availability of diffraction data on three isotopic substituted samples has allowed the extraction of three site–site radial correlation functions (RCF) from [5], while only the so-called total neutron weighted function was available in [4].

Moreover, the differential cross section (DCS) measured in a diffraction experiment is made up of three contributions: two of them derive from the interference of neutrons diffracted by the Vycor glass and water by themselves, and are related to the microscopic structure of the two individual phases; while the third term derives from cross correlations between Vycor glass and water phases. The term coming from the Vycor–Vycor interference can be readily subtracted from the experimental data, if the DCS of the dry Vycor sample is available. The cross correlation term was considered negligible in [4], although this assumption cannot be easily sustained given the relative concentrations of the atomic species, mainly at partial hydration. It has been demonstrated in [5] that each site–site RCF extracted from the experiment (namely $g_{XX}^h(r)$, $g_{XH}^h(r)$ and $g_{HH}^h(r)$, where X labels all non-substituted atoms and h indicates the level of hydration) is indeed a weighted sum of two contributions:

$$\begin{aligned} g_{XX}^h(r) &= a_1^h g_{O_w O_w}(r) + a_2^h g_{O_w X_V}(r) \\ g_{XH}^h(r) &= a_3^h g_{O_w H_w}(r) + a_4^h g_{H_w X_V}(r) \\ g_{HH}^h(r) &= a_5^h g_{H_w H_w}(r) + a_6^h g_{H_w H_V}(r) \end{aligned} \quad (1)$$

where the subscripts O_w and H_w refer to atomic sites belonging to water molecules, X_V and H_V to atomic sites belonging to the SiO_2 molecules of the Vycor substrate and to the H atoms on the pore surface [5]. The a_i^h coefficients depend on the hydration through the atomic concentrations and may also have a radial dependence due to the confinement, as we will discuss [5].

The effects of confinement are indeed the other issue that has been overlooked in [4]. It is known [12, 13] that a straightforward comparison of the site–site RCF of a confined liquid with those of the corresponding bulk may be misleading, because the radial distribution function for the uniform fluid has a structure of its own, purely by virtue of the confinement. The effects of the confinement in the present case are quite intriguing, since the individual atomic species contributing to the site–site correlation functions reported in equation (1) are not confined in the same volume: this is exactly the origin of the r -dependence of the a_i^h coefficients. All of

the details of the data correction for this confinement effect are reported in [5], where it is also demonstrated that the low- r region (~ 0.6 nm) of the RCF is dominated by the water–water correlations, in spite of the small weighting of this term in the average.

If the ansatz now is made that the individual RCF are approximately independent of the hydration level, and measurements have been performed for at least two different hydrations, then it is possible to isolate the $g_{O_w O_w}(r)$, $g_{O_w H_w}(r)$, and $g_{H_w H_w}(r)$ functions appearing in equation (1) from the cross correlation terms. Two of them, namely the $O_w O_w$ and $O_w H_w$, are reported in figures 1(a) and 2(a) for comparison with bulk water data. It is seen that these functions are considerably distorted from their bulk water counterparts. In particular, the first peak in the $O_w O_w$ RCF is lower in amplitude than in the bulk, but now there is a considerable increase in the intensity in the region near 0.3–0.4 nm. This is quite similar to what happens in bulk water when pressure is applied [14, 15], and signals a substantial distortion of the hydrogen bond network. On the other hand, there is still a significant hydrogen bond peak in the $g_{O_w H_w}(r)$ function, although the first minimum is shifted and an extra shoulder appears at $r \sim 0.27$ nm. Even the average number of hydrogen bonds (HB) per molecule is reduced by 50% compared to the bulk water.

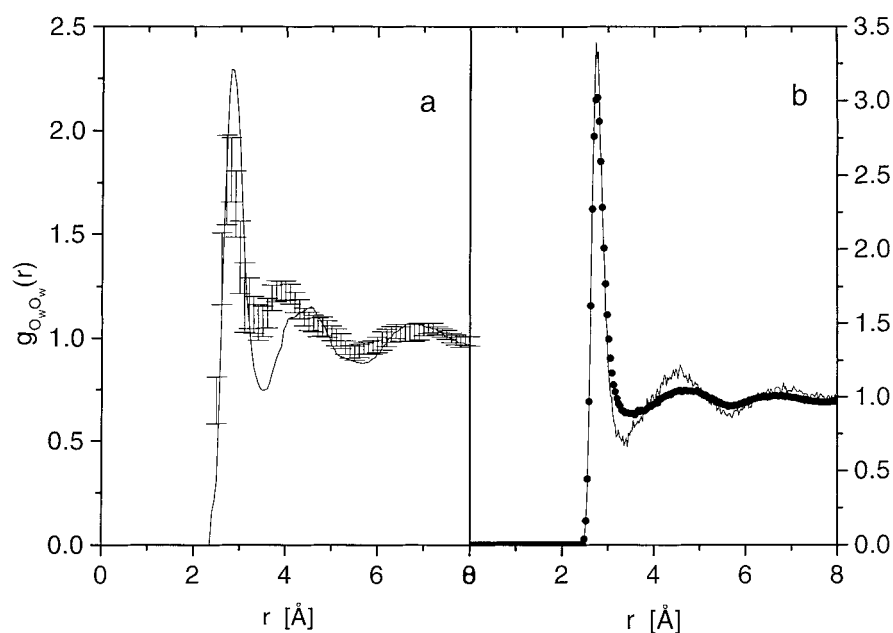


Figure 1. The oxygen–oxygen RCF. (a) Experimental data for bulk water (full curve) and water confined in Vycor glass (error bars) and (b) MD simulations for bulk (full curve) and confined (circles) SPC/E water.

Most of the difficulties inherent in the extraction of the relevant site–site RCF from the experiment do not survive when dealing with MD simulations, since the individual atomic species are labelled by default. It is then possible to analyse the microscopic structure of confined water at various hydration levels in comparison with its bulk counterpart. The confinement effects can be easily accounted for by the form factor of the confining volume, that is a cylinder in the present case for the water substance. More to the point, all of the properties of interest can be analysed separately for the molecules wetting the pore surface and for those belonging to the inner shells. The simulated RCF are compared with those of bulk SPC/E

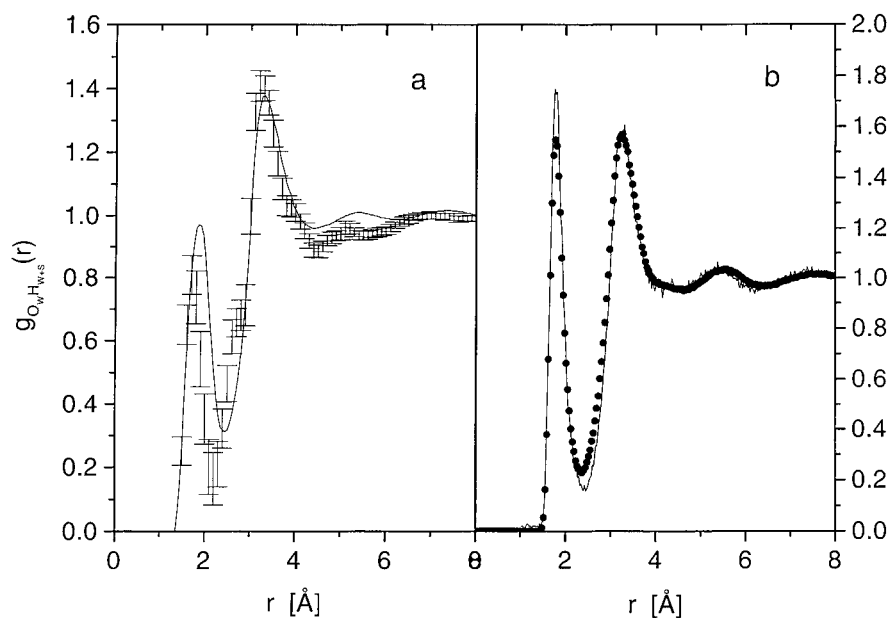


Figure 2. The oxygen–hydrogen RCF using the same symbols as in figure 1.

water at the same density in figures 1(b) and 2(b). We notice that the modifications of these functions upon confinement follow the same qualitative trend observed in the experiment. A deeper analysis of the molecular configurations has demonstrated that this is due to the molecules lying within ~ 0.5 nm of the pore surface, which are considerably less bonded than in the bulk. The distribution of the O–O–O angle between three neighbouring molecules in the middle of the pore is similar to that of bulk water, with a maximum correspondence of the angle characteristic for the tetrahedral coordination; this distribution becomes flat as we proceed towards the pore surface, confirming that the relative orientations of neighbouring molecules are strongly affected by the presence of the hydrophilic surface.

3. Diffusional dynamics

Several quasi-elastic neutron scattering experiments performed on water confined either in Vycor glass or in other hydrophilic environments [1, 8] suggest that the single-particle dynamics in these systems are remarkably similar to each other and are much slower compared with that of bulk water. A common molecular mechanism for the slowing-down of the single-particle dynamics of interfacial water is then considered plausible and in [8, 9] it is proposed that water in the vicinity of a hydrophilic surface is in a state equivalent to supercooled bulk water at a lower temperature. The slowing down of the single-particle dynamics could then be interpreted in the scenario of an approach to the kinetic glass transition. In order to get a better insight into this issue we analysed the dynamics of our SPC/E water confined in the cylindrical Vycor pore at room temperature, focusing the attention on the role of the hydration level [11].

In the inset of figure 3 we show the mean square displacement of the centre of mass motion along the direction of the axis of the cylinder. After an initial ballistic diffusion, at the lower hydration states, the signature of the so-called cage effect is evident, which is absent in room-temperature bulk water. Once the cage formed by the neighbouring molecules has relaxed, water molecules enter the normal diffusive regime.

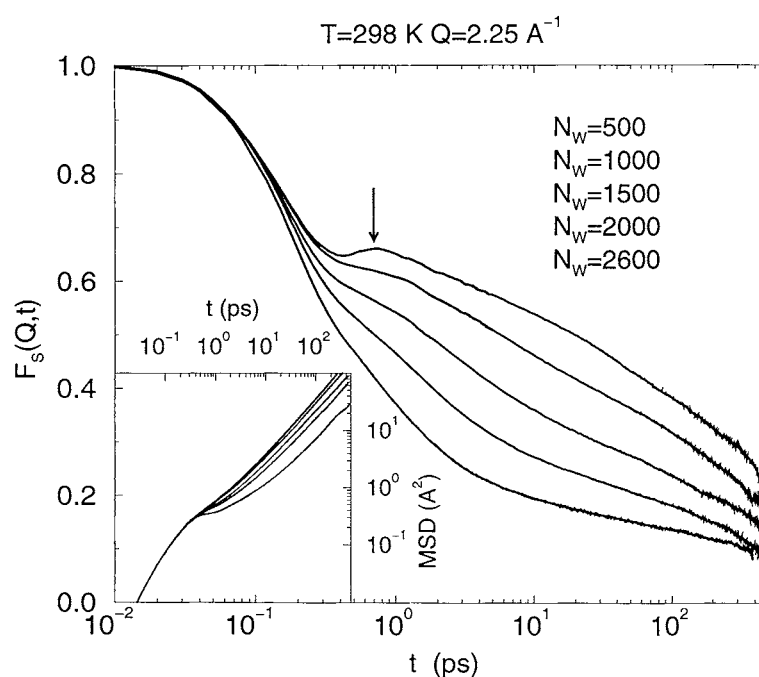


Figure 3. The ISF of room-temperature SPC/E water confined in a cylindrical SiO₂ pore at $Q = 22.5 \text{ nm}^{-1}$ as a function of hydration. The pore hydration decreases from bottom to top: the numbers of water molecules, N_w , correspond to 96%, 74%, 56%, 37%, and 19% of the hydration level of the pore. The arrow indicates the feature related to the boson peak. In the inset the mean square displacement of the centres of mass is shown; the hydration decreases from top to bottom.

The centre of mass motion is then analysed in terms of the intermediate scattering function (ISF) $F_S(Q, t)$, reported in figure 3 at an exchanged wavevector, $Q = 22.5 \text{ nm}^{-1}$, corresponding to the maximum of the oxygen–oxygen structure factor, for all hydration levels investigated. As the hydration level is lowered the ISF displays an increasingly pronounced shoulder at $\sim 1 \text{ ps}$, which is the characteristic of a two-step relaxation process, with highly non-exponential tails at long times: a result similar to that obtained in simulations of bulk SPC/E water upon supercooling [16]. At the lowest hydration an overshooting of the ISF is also visible: this feature is usually related to the so-called boson peak in the density of states of the liquid [17]. When this glassy anomaly appears in a liquid phase, it is considered as a precursor to the actual glass transition. It has to be mentioned that it has recently been demonstrated that a stretched exponential-relaxation description of the long-time dynamics of the single molecule is consistent with high-resolution, low- Q neutron scattering data of water confined in Vycor glass [9]. The possible existence of a boson peak, on the contrary, is still an open question and experiments are scheduled for the near future.

4. Conclusions

It has been demonstrated by experiments and MD simulations that the microscopic structure of water confined in a hydrophilic substrate, for instance porous Vycor glass, is strongly distorted in comparison with bulk water. In particular, the water layers closer to the substrate form less HB and are not tetrahedrally coordinated: a circumstance that can prevent nucleation of ice I_h

and allow easy supercooling. Moreover, the guess that confining water in small hydrophilic pores is analogous, from the dynamical point of view, to supercooling is now sustained by MD results.

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