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Strong layering effects and anomalous dynamical behaviour in confined water at low hydration

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Abstract

Molecular dynamics results on water confined in a silica pore in the low-hydration regime are presented. Strong layering effects are found due to the hydrophilic character of the substrate. The local properties of water are studied as a function of both temperature and hydration level. The interaction of the thin films of water with the silica atoms induces a strong distortion of the hydrogen bond network. The residence time of the water molecules is dependent on the distance from the surface. Its behaviour shows a transition from a Brownian to a non-Brownian regime on approaching the substrate in agreement with results found in studies of water in contact with globular proteins. The confined liquid at low hydration shows upon supercooling an anomalous behaviour which is rather different to that in the high-hydration regimes already studied.

1. Introduction

In many systems of interest for technological and biophysical problems, water is confined by or in contact with surfaces. There are a number of important processes in Nature where water confined in microcavities plays an important role [1]. Several experiments have been performed in the last ten years using different techniques and different confining substrates. They have evidenced various behaviours of the confined water [2]. It is still difficult however to make predictions on one hand on the role of water in influencing the behaviour of the substrate and on the other hand on the role of the substrate in modifying the properties of water. It has been observed by means of computer simulation that the density profile of water in restricted geometries is not uniform [3–5]. In a recent computer simulation of SPC/E water confined in a model of porous silica the formation of two distinct layers of water with different structural and dynamical properties has been observed [6–8]. In the layer far from the surface, the water shows a behaviour similar to that of bulk water, but in the layer close to the substrate there is a strong reduction of the tetrahedral order with a consequent distortion of the hydrogen bond (HB) network, as observed in experiments performed on water confined in Vycor [9, 10] and other hydrophilic environments [11, 12]. In the layer close to the substrate, moreover, one

observes a strong reduction of the mobility of the molecules [6–8]. There is experimental evidence of a slow relaxation of water in contact with proteins [13, 14] and water confined in Vycor for low hydrations [15].

In this paper we focus on a molecular dynamics study of confined water in a low-hydration regime. This regime is very relevant for making connection with experiments and for a better understanding of the effects of the substrate on the water properties.

2. Density profiles and the hydrogen bond in confined water

The computer simulation is performed on SPC/E water inserted in a cylindrical cavity of radius 20 Å carved in a cubic cell of silica glass obtained by computer simulation [4]. The internal surface of the cavity is modelled to represent a substrate of Vycor glass and it is composed of silicon atoms (Si), bridging oxygens (BO) bonded to two silicons and non-bridging oxygens (NBO) connected to only one silicon. The NBO are saturated with acidic hydrogens (AH). The interaction of water with the substrate is modelled by assigning different charges to the sites representing the atoms of Vycor. A Lennard-Jones interaction between the oxygens of water and the BO and NBO of the confining system is assumed [4]. Periodic boundary conditions are applied along the axis of the cylinder assumed as the z -direction. The motion is confined in the xy -plane, where the distance from the axis is defined in terms of the radius $R = \sqrt{x^2 + y^2}$. During the simulation the substrate is kept rigid.

The full hydration density in experiments [9], 0.0297 \AA^{-3} , corresponds to roughly $N_W = 2600$ molecules. We performed our simulation at three different hydration levels: $N_W = 500$ (19% hydration), $N_W = 1000$ (38%) and 1500 (58%).

In figure 1 we report the density profiles along the pore radius and the profiles of the HB per molecule. The hydrophilic effects of the substrate are evident in the double-layer structure in the zone $15 < R < 20 \text{ \AA}$ and the formation of HB between atoms of the surface (mainly BO) and the water molecules [16]. At the highest hydration ($N_W = 1500$) the density in the double-layer structure increases above the value of the density of water in ambient conditions. It is evident that the decrease of temperature does not have much effect on the density profiles. The number of water–water HB $N_{ww}^{HB}(R)$ increases along the pore radius and reaches a maximum at $R = 16 \text{ \AA}$, which corresponds to the minimum in the density profiles. At this distance, which is roughly 4 Å from the surface, the water–Vycor HB start to substitute for the water–water HB, so the total number of HB $N_{tot}^{HB}(R) = N_{ww}^{HB}(R) + N_{wv}^{HB}(R)$ remains almost constant along the profile. The temperature has little effect on the HB profiles. We observe also that few molecules penetrate inside the substrate; they do not give any contribution to the dynamics of the system.

A layer analysis of the local arrangement of the nearest-neighbour molecules and the local tetrahedral order along the pore shows that while a good short-range order is present for all the hydrations in the layer $0 < R < 16 \text{ \AA}$ where the water molecules form HB with almost all their neighbours, in the layer closest to the Vycor surface, $16 < R < 18 \text{ \AA}$, the tetrahedral arrangement is completely lost due to the formation of HB between water molecules and the substrate [16]. These results are in agreement with experimental studies on water confined in Vycor [9, 10] and in contact with other surfaces [11].

3. Residence time and diffusion

The interaction with the substrate affects the dynamics of the molecules as is evident in the average residence times shown in figure 2 along the pore radius. For all hydrations we observe

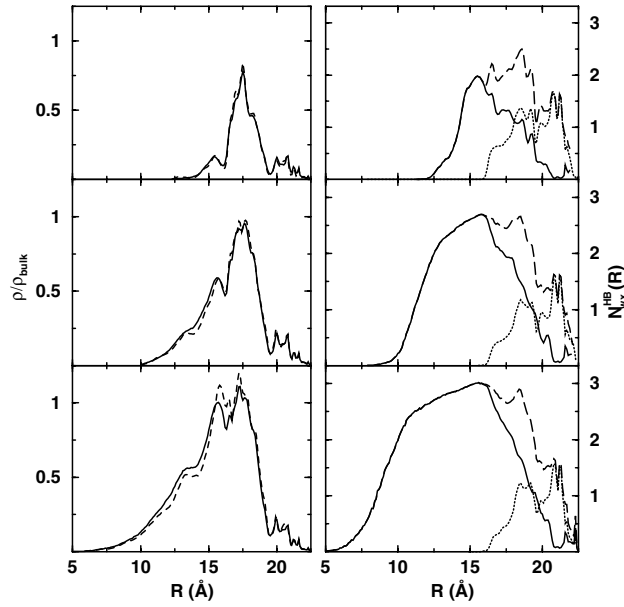


Figure 1. Density profiles (on the left) and average number of HB per molecule (on the right) along the pore radius for $N_W = 500$ (top), $N_W = 1000$ (middle), $N_W = 1500$ (bottom). The density is normalized to the value for water at ambient temperature $\rho_{bulk} = 0.0334 \text{ \AA}^{-3}$ and it is reported for the temperatures $T = 300$ K (solid curve), $T = 220$ K (dotted curve). The number of HB is calculated at $T = 300$ K using a geometrical criterion; see [16]. The solid curve represents the water–water $N_{ww}^{HB}(R)$, the dotted curve is the water–Vycor $N_{wv}^{HB}(R)$ and the long-dashed curve is the total $N_{tot}^{HB}(R)$.

oscillations which are more enhanced for $N_W = 500$. The residence times reach maximal values where the molecules are attached at the Vycor surface; for the rest they are strongly determined by the double-layer structure. At each hydration along the pore, the residence time reaches higher values where the density profile exhibits local maximal values, while the residence time minimum is found roughly at the minimum of the density distribution between the two layers. We can infer by comparing figures 1 and 2 that the HB formed in the zone of minimum density are not stable, since the water molecules reside there for a shorter time than in the region of the maxima of the double-layer structure. The enhancement of the residence time maxima with decreasing hydration can be explained in terms of an increase in the rigidity of the HB. In fact, with decreasing hydration one observes an increase of the number of nearest-neighbour molecules which form HB [16].

From the calculations of the residence time we can obtain the distributions $\mathcal{P}(t)$ shown in figure 3 for the case $N_W = 1000$ at room temperature.

For the layer close to the surface we can fit the distribution with a power law function $\mathcal{P}(t) = at^{-\mu}$ where the exponent μ assumes slightly different values for the layer $16 < R < 20 \text{ \AA}$ $\mu = 1.42$ and for the layer $14 < R < 20 \text{ \AA}$ $\mu = 1.36$. In the inset of the same figure it is evident that the residence time distribution for the internal layer $0 < R < 16 \text{ \AA}$ shows a long-time decay following an exponential law.

The power law behaviour of the residence time distribution indicates an anomalous dynamical behaviour of the molecules. In a recent neutron scattering experiment and MD simulation on water in contact with a globular protein [14] similar results have been found, with a distribution of the residence times of the water molecules in the layers close to the

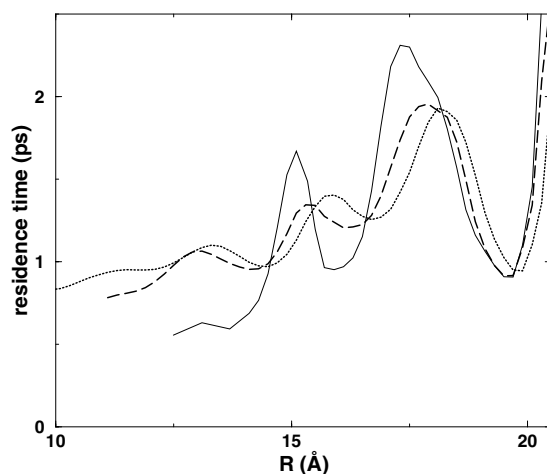


Figure 2. The average residence time of the water molecules along the pore radius for $T = 300$ K at different hydrations: $N_W = 500$ (solid curve), $N_W = 1000$ (long-dashed curve), $N_W = 1500$ (dotted curve).

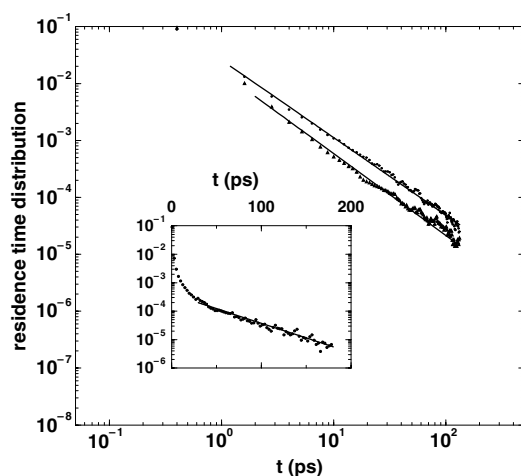


Figure 3. The residence time distribution at room temperature for $N_W = 1000$ for the layers $16 < R < 20$ Å (triangles) and $14 < R < 20$ Å (circles); the solid curves are power law fits (see the text). In the inset we show the result for the layer $0 < R < 16$ Å with the fit to an exponential law (solid curve).

protein surface fitted to a power law while an exponential decay is found for the distribution of the residence times of water molecules far from the protein surface [14].

The anomalous dynamical behaviour is more evident in the mean square displacement reported in figure 4 for $N_W = 500$ calculated for decreasing temperatures. We observe after an initial ballistic regime the presence of a plateau indicating the onset of a cage effect, which becomes more evident with decreasing temperatures. The cage effect in confined water has been found at higher hydrations in previous work [7, 8], but now after the plateau we do not observe the onset of a Brownian dynamics. The long-time behaviour of the mean square displacement can be fitted with a sublinear power law behaviour, $\langle r^2(t) \rangle \propto t^\alpha$ with $\alpha < 1$.

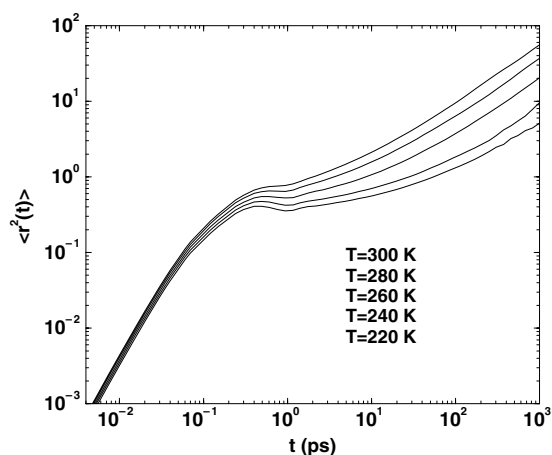


Figure 4. Mean square displacement as a function of time for $N_W = 500$ with temperature decreasing from top ($T = 300$ K) to bottom ($T = 220$ K).

4. Conclusions

We have studied by means of computer simulation the structural and dynamical properties of a model for water confined in Vycor. We have considered the low-hydration regime. Water molecules form a double-layer structure of 4–5 Å close to the surface, where the local properties of water are strongly affected by the interaction with the substrate.

The HB network is deformed with respect to that of bulk water, in agreement with experimental results.

The layer analysis of the residence time of the water molecules along the pore radius shows a clear connection between this quantity and the density profiles.

The residence time distribution decays exponentially in the layer far from the surface, but it shows an anomalous non-Brownian behaviour in the layers close to the substrate with a power law decay for long times. Non-Brownian dynamics is evident from the mean square displacement at the lowest hydration explored where there is also evidence of the onset of a cage effect on lowering the temperature below the ambient value. The results obtained are in agreement with the behaviour of water in contact with a globular protein. A more refined analysis of the dynamical properties of confined water in the low-hydration regime is in progress.

References

- [1] Debenedetti P G 1977 *Metastable Liquids: Concepts and Principles* (Princeton, NJ: Princeton University Press)
- Robinson G W *et al* 1996 *Water in Biology, Chemistry and Physics* (Singapore: World Scientific)
- Israelachvili J and Wennerstrom H 1996 *Nature* **379** 219
- [2] See for instance:
 - Ricci M A and Rovere M 2000 *J. Physique IV* **10** 187
 - Ricci M A, Bruni F, Gallo P, Rovere M and Soper A K 2000 *J. Phys.: Condens. Matter* **12** A345
- [3] Lee S H, McCammon J A and Rosky P J 1984 *J. Chem. Phys.* **80** 4448
- Lee S H and Rosky P J 1994 *J. Chem. Phys.* **100** 3334
- Spohr E 1997 *J. Chem. Phys.* **106** 338
- Fang J X *et al* 1997 *J. Chem. Phys.* **107** 5212
- Zhu S B and Robinson G W 1991 *J. Chem. Phys.* **94** 1403

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- [4] Spohr E, Hartnig C, Gallo P and Rovere M 1999 *J. Mol. Liq.* **80** 165
 - [5] Hartnig C, Witschel W, Spohr E, Gallo P, Ricci M A and Rovere M 2000 *J. Mol. Liq.* **85** 127
 - [6] Gallo P, Rovere M, Ricci M A, Hartnig C and Spohr E 2000 *Europhys. Lett.* **49** 183
 - [7] Gallo P, Rovere M and Spohr E 2000 *Phys. Rev. Lett.* **85** 4317
 - [8] Gallo P, Rovere M and Spohr E 2000 *J. Chem. Phys.* **113** 11324
 - [9] Bruni F, Ricci M A and Soper A K 1998 *J. Chem. Phys.* **109** 1478
 - [10] Soper A K, Bruni F and Ricci M A 1998 *J. Chem. Phys.* **109** 1485
 - [11] Raviv U, Laurat P and Klein J 2001 *Nature* **413** 51
 - [12] Bergman R and Svenson J 2000 *Nature* **403** 283
Bergman R, Svenson J, Börjesson L and Jacobsson P 2000 *J. Chem. Phys.* **113** 357
 - [13] Settles M and Doster W 1996 *Faraday Discuss. Chem. Soc.* **103** 269
 - [14] Rocchi C, Bizzarri A R and Cannistraro S 1998 *Phys. Rev. E* **57** 3315 and references therein
Paciaroni A, Bizzarri A R and Cannistraro S 2000 *Phys. Rev. E* **62** 3991
 - [15] Venturini F, Gallo P, Ricci M A, Bizzarri A R and Cannistraro S 2001 *J. Chem. Phys.* **114** 10010
 - [16] Gallo P, Rapinesi M and Rovere M 2002 *J. Chem. Phys.* **117** 369