Anomalous dynamics of confined water at low hydration.

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The mobility of water molecules confined in a silica pore is studied by computer simulation in the low hydration regime, where most of the molecules reside close to the hydrophilic substrate. A layer analysis of the single particle dynamics of these molecules shows an anomalous diffusion with a sublinear behaviour at long time. This behaviour is strictly connected to the long time decay of the residence time distribution analogously to water at contact with proteins.

I. INTRODUCTION

Water plays a major role in many different biological, chemical and physical phenomena. In most of these cases a large fraction of water is at contact with different substrates and its motion is restricted in small spaces.

It is expected that both the geometrical confinement and the interaction with the substrate perturb the structural and dynamical properties of water and some general trends have been found in experiments and computer simulation.

In many phenomena, like those connected with biological matter, it is of great relevance the behaviour of the shells of water close to substrates. In particular the slow dynamics of water close to the surfaces of proteins might play a fundamental role in the protein functionality and evidences have been found of a glasslike behaviour of water at contact with plastocyanin investigated in a wide temperature range by computer simulation.

Water confined in Vycor glass is a good prototype system for studying the effect of an hydrophilic substrate since the surface of Vycor pores is well characterized. In particular experimental studies with quasi-elastic neutron scattering and neutron resonance spin-echo on confined water indicated a slowing down of the dynamics with respect to the bulk and a study focused on the low hydration regime has evidenced upon supercooling the existence of a low frequency scattering excess typical of strong glass formers.

In computer simulations of water confined in a pore of Vycor glass we found that strong layering effects are present where the molecules close to Vycor glass show very slow dynamics even at ambient temperature. In a more focused study on the low hydration regime we recently performed also a preliminary study of the residence time (RT) of the water molecules. We found that the RT is strongly dependent on the distance from the substrate and its distribution shows an anomalous non-brownian behaviour when the contribution of the molecules close to the substrate alone is considered.

The aim of this paper is to show the connection between the anomalous behaviour of the RT and the long time limit of the mean square displacement (MSD) in the low hydration regime. The paper is structured as follows: in the next section we briefly describe the system, give details of the computer simulation and discuss some structural properties of confined water useful for the characterization of the RT behaviour. In the third section by considering the residence time distribution and the molecular diffusion we show the onset of an anomalous behaviour connected to the presence of the solid disordered substrate. The last section is devoted to conclusions.

II. STRUCTURAL PROPERTIES OF CONFINED WATER

The molecular dynamics (MD) calculations have been performed in a cell of silica glass previously obtained by the usual quenching procedure.

Inside the glass cubic cell of 71 Å a cylindrical cavity of 40 Å diameter has been carved. The surface of the cavity has been treated to reproduce the average properties of the surface of the pores of Vycor. Along this line hydrogen ions (acidic hydrogens) have been added to oxygens non saturated by silicon in order to mimic the procedure followed by experimentalists in the preparation of the Vycor sample before hydration. The surface of silica glass can be considered as a prototype model for a disordered hydrophilic substrate. Being primarily interested in the dynamics of water the substrate is kept rigid. The water inserted in the cavity is simulated by using the SPC/E potential, where each molecule is represented by three charged sites. These sites interact also with the silicon and oxygen atoms of the substrate by means of an hydrophilic potential described in previous work. The molecular dynamics (MD) is performed at different hydrations by varying the number of water molecules contained in the pore. For each hydration the system is equilibrated at different temperatures. The quantities of interest presented in the following are averaged over runs that extend up to 1.2 – 1.3 ns. We note that we have extended the simulation length at all temperatures with respect to ref. to improve statistics especially on the computation of the RT.

The number of water molecules considered in this work are \( N_W = 500 \), \( N_W = 1000 \), \( N_W = 1500 \), which corre-
FIG. 1: For \(N_W = 1500\) water molecules at \(T = 300\) K along the cylindrical radius \(R\) are shown: at the bottom density profiles along the cylindrical radius \(R\) at \(T = 300\) K normalized to the density of bulk water at ambient conditions; in the middle number of hydrogen bonds (HB) per molecule, the bold line represents the water-water HB, the dotted line the water-Vycor HB; at the top residence time along the cylindrical radius \(R\).

FIG. 2: For \(N_W = 1000\) water molecules at \(T = 300\) K along the cylindrical radius \(R\) are shown: at the bottom density profiles along the cylindrical radius \(R\) at \(T = 300\) K normalized to the density of bulk water at ambient conditions; in the middle number of hydrogen bonds (HB) per molecule, the bold line represents the water-water HB, the dotted line the water-Vycor HB; at the top residence time along the cylindrical radius \(R\).

FIG. 3: For \(N_W = 500\) water molecules at \(T = 300\) K along the cylindrical radius \(R\) are shown: at the bottom density profiles along the cylindrical radius \(R\) at \(T = 300\) K normalized to the density of bulk water at ambient conditions; in the middle number of hydrogen bonds (HB) per molecule, the bold line represents the water-water HB, the dotted line the water-Vycor HB; at the top residence time along the cylindrical radius \(R\).

spond to hydration levels of the pore of 19\%, 38\% and 56\% respectively, since the density corresponding to the full hydration in the experiments \(\rho = 0.878\) g/cm\(^2\) is obtained in our geometry for \(N_W = 2600\).

The effects of the hydrophilic interaction of the substrate on the water molecules are shown in the bottom panels of Fig. 1, 2 and 3 for the different hydrations. The radial density profiles normalized to the density of bulk water at ambient conditions show the formation of two layers of molecules close to the substrate. The positions of the peaks of the double layer structure do not change with hydrations, the first layer is located at around \(R \approx 17.5\) Å and the second layer is at \(R \approx 15.5\) Å with a minimum in the density at \(R \approx 16\) Å. The heights of the peaks increase with increasing hydrations and for \(N_W = 1500\) the normalized density profile for confined water in the layers reaches values higher than one at ambient temperature.

In the middle panels of Fig. 1, 2 and 3 it is shown that the intermolecular hydrogen bond (HB) profiles increase and reach a maximum value at the position of the minimum of density \((R \approx 16\) Å\) where they start to go down in correspondence with the increase of the HB of water molecules with the atoms of the Vycor surface. The layering effect shown in the bottom panels is due to the formation of the Vycor-water HB. We found that the temperature has little effects on the density and HB profiles at all the hydration levels and for this reason
we show here only the results corresponding to ambient temperature.

III. RESIDENCE TIME AND ANOMALOUS DIFFUSION

At the top of Fig. 1, 2 and 3 the residence times (RT) of the water molecules at ambient temperature are reported along the pore radius. The large oscillations of the RT appear modulated by the structure of the density profiles, reported in the bottom panels of the same figures. Apart for the molecules attached to the surface water resides for the longer time inside the shells, where the density profile reaches the highest values. The minima of the RT are located close to the minima of the density profiles.

In Fig. 4 are reported the calculations of the mean square displacement (MSD) at $N_W = 1000$ for decreasing temperatures. It is clear that after the ballistic regime at short time, at around 0.1 ps there is the onset of a cage effect characterized by the presence of a plateau which increases by lowering the temperature. The plateau is determined by the transient caging of the nearest neighbours. At longer times the MSD does not appear to reach the usual Brownian diffusion since the behaviour is sub-linear. Analogous results are found for the other hydration levels investigated. At this point further analysis is needed in order to clarify whether this subdiffusive behaviour is just a transient leading to normal Brownian diffusion for longer times, although unachievable with normal computers, or it can be framed in the context of anomalous subdiffusive phenomena.

Anomalous diffusion is generally speaking defined trough the time dependence of the MSD, the second moment of the spatial coordinates of the diffusive particles, which generally has a long time dependence of the form

$$< r^2(t) > = a t^{\alpha}$$  \hspace{1cm} (1)

Anomalous diffusion corresponds to $\alpha \neq 1$. In particular $\alpha > 1$ is termed superdiffusion and $\alpha < 1$ subdiffusion. From a theoretical point of view the origin of anomalous diffusion can be traced back to the analytic form of the distribution of the waiting times $\psi(t)$. Under the assumption that the amplitude of the random jumps is constant and finite anomalous diffusion has been shown to be generated by an inverse power law distribution for large times.\textsuperscript{16,17}

$$\psi(t) = A t^{-\mu}$$  \hspace{1cm} (2)

In the case of ordinary brownian motion the long time limit of the distribution would decay with an exponential law.

In our case the sublinear diffusion observed can be connected to the processes which take place close to the substrate and to the interaction of the water molecules with the disordered surface. In this respect since oscillations of the RT appear so closely connected to the double layer structure it is of interest to look at the residence time distribution of the water molecules close to the substrate.

In Fig. 4 and 5 we report the residence time distributions (RTD) $\psi(t)$ at the highest $T = 300$ K and the lowest $T = 240$ K temperatures investigated for $N_W = 1000$ and $N_W = 1500$ . The RTD, calculated for the molecules in the layer $14 < R < 20$ Å, shows the predicted power law behaviour of Eq. 2 while for the rest of the molecules we get an exponential decay, as shown in the inset of the figures. The power law behaviour related to the temporal disorder of the distribution of the residence times of the molecules has been observed in computer simulation and experiments on water at contact with proteins.\textsuperscript{14} They are specifically related to the interaction of the solvent with the protein sites.

The power law decay of the RTD of the molecules in the 6 Å layer from the surface is determined by values of the exponents which are similar to the ones obtained for the RTD of water in few Å shells close to protein hydration sites. In particular for the case $N_W = 1000$ we have $\mu = 1.54 \pm 0.05$ at $T = 300$ K and $\mu = 1.50 \pm 0.05$ at $T = 240$ K, while for $N_W = 1500$ the fits yield $\mu = 1.50 \pm 0.05$ at $T = 300$ K and $\mu = 1.52 \pm 0.05$ at $T = 240$ K. We note that the present result for $\mu$ at $N_W = 1500$ and ambient temperature is slightly different from the preliminary one reported in ref.\textsuperscript{14}, where the statistics was poorer.

The sublinear behaviour of the MSD is connected to the power law decay of the RTD by the asymptotic temporal dependence

$$< r^2(t) > \propto t^{\mu - 1}$$  \hspace{1cm} (3)

From the fit of the long time behaviour of the MSD for $N_W = 1000$ and $N_W = 1500$, reported in Fig. 7 and Fig. 8 we get the values of the exponent $\mu$ which are...
FIG. 5: Log-log plot of the residence time distribution (RTD) of the water molecules in the layer $14 < R < 20$ Å for $N_W = 1000$ at temperatures $T = 300$ K (open triangles) and $T = 240$ K (open squares). The fits (bold lines) are done with a power law $A t^{-\mu}$. $A = 0.059$, $\mu = 1.54 \pm 0.05$ at $T = 300$ K. $A = 0.021$, $\mu = 1.50 \pm 0.05$ at $T = 240$ K. In the inset are shown in a linear-log scale the RTD for the molecules in the layer $0 < R < 14$ Å.

FIG. 6: Log-log plot of the residence time distribution (RTD) of the water molecules in the layer $14 < R < 20$ Å for $N_W = 1500$ at temperatures $T = 300$ K (open triangles) and $T = 240$ K (open squares). The fits (bold lines) are done with a power law $A t^{-\mu}$. $A = 0.059$, $\mu = 1.50 \pm 0.05$ at $T = 300$ K. $A = 0.026$, $\mu = 1.52 \pm 0.05$ at $T = 240$ K. In the inset are shown in a linear-log scale the RTD for the molecules in the layer $0 < R < 14$ Å.

FIG. 7: MSD of water molecules in the layer $14 < R < 20$ Å for $N_W = 1000$ at temperatures $T = 300$ K and $T = 240$ K from above. The long dashed lines are the fits to a sublinear behaviour $< r^2 > \propto t^\alpha$ with $\alpha = 0.46 \pm 0.05$ at $T = 300$ K and $\alpha = 0.48 \pm 0.05$ at $T = 240$ K. In the inset are reported the functions $< r^2 > / t$.

FIG. 8: MSD of water molecules in the layer $14 < R < 20$ Å for $N_W = 500$ at $T = 300$ K and $T = 240$ K from above. The long dashed lines are the fits to a sublinear behaviour $< r^2 > \propto t^\alpha$ with $\alpha = 0.46 \pm 0.05$ at $T = 300$ K and $\alpha = 0.48 \pm 0.05$ at $T = 240$ K. In the inset are reported the functions $< r^2 > / t$.

In the lower hydration case $N_W = 500$, Fig. 8, the RTD decays for long time with an exponent similar to the previous cases, $\mu = 1.45 \pm 0.05$ and $\mu = 1.55 \pm 0.05$ for $T = 300$ K and $T = 240$ K respectively, but the MSD show, as seen in the inset of Fig. 8, a long time behaviour not in agreement with the one predicted by Eq. 3.

The asymptotic behaviour of the MSD shows a further slowing down with respect to the higher hydrations. This behaviour is likely connected to the fact that the water molecules are arranged in clusters close to the substrate.

IV. CONCLUSIONS

The dynamical properties of confined water are expected to be changed by the interaction with the substrate. We performed computer simulation of water molecules confined in a silica pore in low hydration regimes, where the larger amount of water resides in the shells closer to the hydrophilic surface. We found drastic changes of the diffusion of the water molecules. From a layer analysis for the investigated hydrations we find that the diffusive regime at long time of the molecules close to the substrate is characterized by a sublinear trend.

Anomalous diffusion phenomena are related to a temporal disorder typical of particles which diffuse close to and interact with a disordered surface. Different interaction processes between the water molecules and the

consistent with the exponents obtained from the power law behaviour of the RTD seen in Fig. 5 and Fig. 6.

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sites of the substrate modulate the residence time of the molecules. A dispersive transport regime related to temporal disorder shows up in the power law decay of the residence time distribution with an exponent which determines also the long time tail of the mean square displacement. In our system the exponent of the long time behaviour of the mean square displacement is related to the long time decay of the residence time distribution of the molecules in the same layer for the cases $N_W=1500$ and $N_W=1000$ as theoretically predicted. For the lowest hydration case ($N_W=500$) the mobility of the molecules is more strongly modulated by the substrate with respect to the higher hydrations. The formation of clusters of molecules close to the solid surface does not appear to modify the long time decay of the RTD but it induces a further slowing down of the dynamics with a violation of the expected behaviour of the MSD.

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