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Anomalous dynamics of confined water at low hydration

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Abstract

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 over a long period. This behaviour is strictly connected to the long time decay of the residence time distribution analogous to water in contact with proteins.

1. Introduction

Water plays a major role in many different biological, chemical and physical phenomena [1–3]. In most of these cases a large fraction of water is in 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 [4].

In many phenomena, like those connected with biological matter, the behaviour of the shells of water close to substrates is of great relevance. In particular the slow dynamics of water close to the surfaces of proteins might play a fundamental role in the protein functionality and evidence has been found of a glass-like behaviour of water in contact with plastocyanin investigated in a wide temperature range by computer simulation [5].

Water confined in Vycor glass is a good prototype system for studying the effect of a hydrophilic substrate since the surface of Vycor pores is well characterized [6]. In particular experimental studies with quasi-elastic neutron scattering and neutron resonance spin-echo [7, 8] 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 a strong glass former [9].

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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 the Vycor glass show very slow dynamics, even at ambient temperature [10–12]. The dynamical properties of confined water have been interpreted in terms of a layer analysis. It has been shown at full and half hydration that water molecules which reside in a layer of 4 Å close to the substrate (bound water) have a very slow dynamics as compared with the rest of the water inside the pore (free water). The dynamical properties of free water upon supercooling have then been analysed in more detail. In particular in the mean square displacement (MSD) of free water upon supercooling, one can distinguish three different temporal regimes. At very short times one observes the ballistic regime, after that a plateau connected to the cage effect appears for intermediate times. When the cage relaxes the particle can diffuse and the usual Brownian regime takes over so that the MSD shows a linear behaviour at very long times.

In previous work the dynamical properties of the molecules close to the substrate were not analysed. These molecules play, of course, a more relevant role at low hydration. In a more focused study on the low hydration regime [4, 13, 14], we recently performed a preliminary study of the residence time (RT). We found that the RT is strongly dependent on the distance of the molecules 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.

In this paper we take into consideration mainly the dynamical properties of the water molecules which are in the layers close to the substrate. The aim is to show the connection between the anomalous behaviour of the RT and the long time limit of 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 [13] useful for the characterization of the RT behaviour. In the third section by considering the RT 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.

2. 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 [15].

Inside the glass cubic cell of 71 Å a cylindrical cavity of 40 Å diameter has been carved so that we eventually have a cylindrical cavity with a radius of 20 Å. The surface of the cavity has been treated to reproduce the average properties of the surface of the pores of Vycor so that finally the surface of the substrate is composed of silicons, bridging oxygens, which are bonded to two silicons, and non-bridging oxygens connected only to one silicon. Hydrogen ions (acidic hydrogens) have been added to non-bridging oxygens 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 also interact with the silicon and oxygen atoms of the substrate by means of a hydrophilic potential described in previous work [11, 15]. The MD is performed at different hydrations by varying the number of water molecules contained in the pore. Periodic boundary conditions are applied along the axis of the cylinder assumed as the z direction. The motion of the molecules is confined in the xy plane. The distance from the axis is defined by means of the radius $R = \sqrt{x^2 + y^2}$. We note that R is not restricted to be less than 20 Å since few molecules penetrate inside the substrate. For each hydration

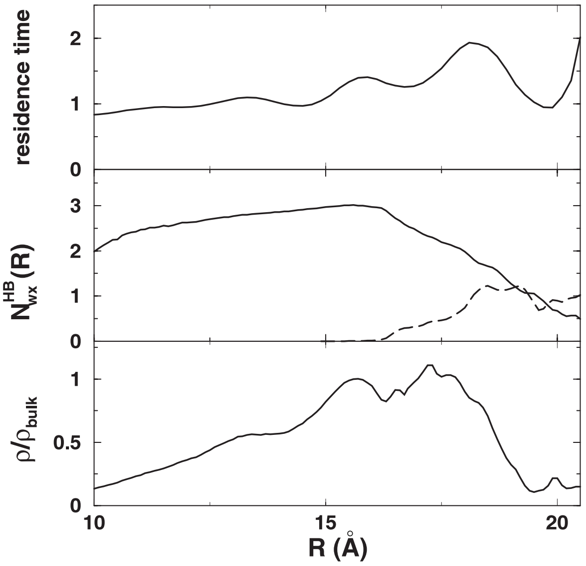

Figure 1. The distance from the cylindrical axis R for $N_W = 1500$ water molecules at $T = 300$ K. Bottom: density profiles at $T = 300$ K normalized to the density of bulk water at ambient conditions; middle: number of HBs per molecule, the bold curve represents the water–water HB, the dashed curve the water–Vycor HB; top: RT.

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 [13] to improve statistics especially on the computation of the RT.

The number of water molecules considered in this work are $N_W = 500$, 1000 and 1500, which correspond 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 figures 1–3 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 $R = 17.5$ 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.

The middle panels of figures 1–3 show the number of hydrogen bonds (HBs) per molecule. Two water molecules are considered neighbours if their O–O separation is less than 3.35 Å. Moreover they are hydrogen bonded if the H–O $\cdots$ O angle is less than 30°. It is shown that the intermolecular 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 in the number of HBs 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 effect 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.

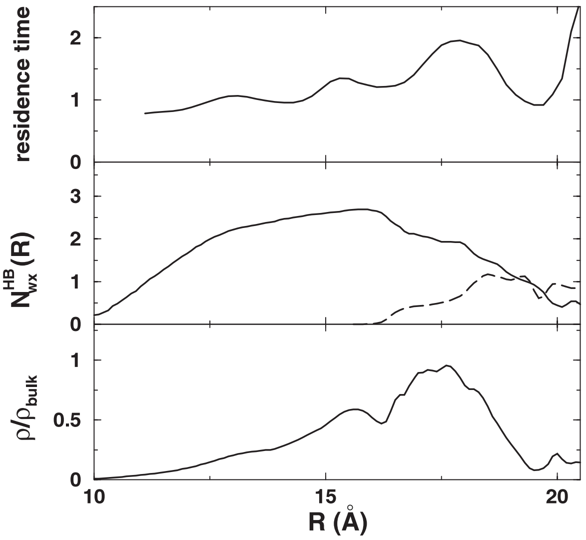

Figure 2. The distance from the cylindrical axis R for $N_W = 1000$ water molecules at $T = 300$ K. Bottom: density profiles at $T = 300$ K normalized to the density of bulk water at ambient conditions; middle: number of HBs per molecule, the bold curve represents the water–water HB, the dashed curve the water–Vycor HB; top: RT.

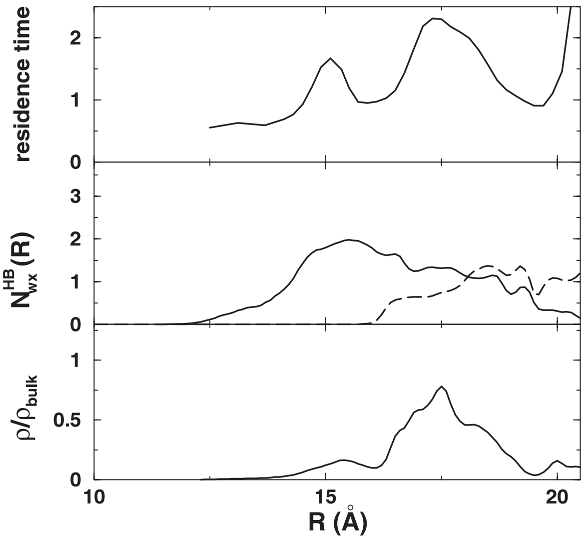

Figure 3. The distance from the cylindrical axis R for $N_W = 500$ water molecules at $T = 300$ K. Bottom: density profiles at $T = 300$ K normalized to the density of bulk water at ambient conditions; middle: number of HBs per molecule, the bold curve represents the water–water HB, the dashed curve the water–Vycor HB; top: RT.

3. Residence time and anomalous diffusion

At the top of figures 1–3 the RT of the water molecules at ambient temperature are shown along the pore radius [13]. 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 from the molecules

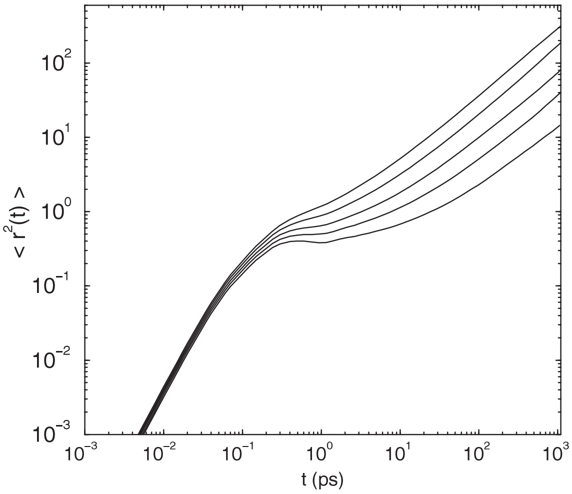

Figure 4. MSD for $N_W = 1000$ at decreasing temperature: $T = 300$, 280, 260, 240 and 220 K from the top.

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 RTs are located close to the minima of the density profiles.

Figure 4 shows the calculations of the 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 sublinear. 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 unreachable with normal computers, or it can be framed in the context of anomalous subdiffusive phenomena.

Anomalous diffusion is generally speaking defined through 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

$$\langle r^2(t)\rangle = at^{\alpha}. \tag{1}$$

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 [16, 17]

$$\psi(t) = At^{-\mu}. \tag{2}$$

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 [18]. 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 RT distribution of the water molecules close to the substrate.

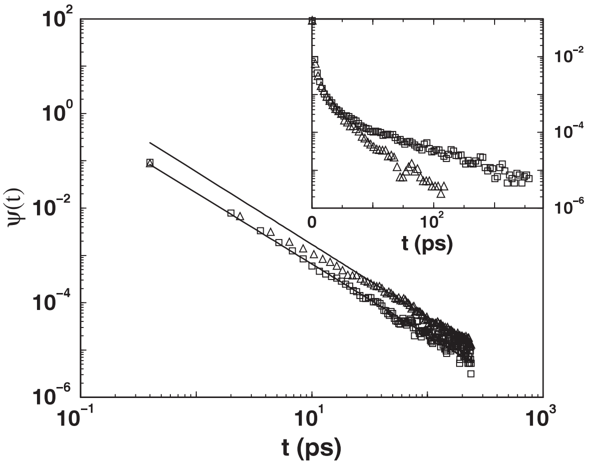

Figure 5. Log–log plot of the RTD of the water molecules in the layer 14 Å $< R <$ 20 Å for $N_{\mathrm{W}} = 1000$ at temperatures $T = 300$ K (open triangles) and $T = 240$ K (open squares). The fits (bold lines) are done with a power law $At^{-\mu}$. $A = 0.059$, $\mu = 1.54 \pm 0.05$ at $T = 300$ K. $A = 0.021$, $\mu = 1.50 \pm 0.05$ at $T = 240$ K. In the inset, in a linear–log scale, the RTD for the molecules in the layer 0 Å $< R <$ 14 Å are shown.

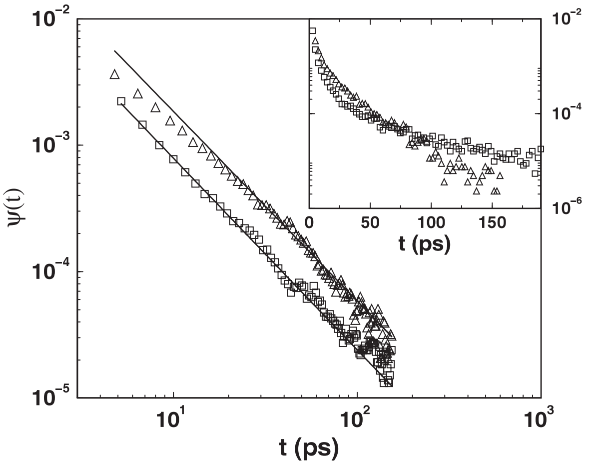

Figure 6. Log–log plot of the RTD of the water molecules in the layer 14 Å $< R <$ 20 Å for $N_{\mathrm{W}} = 1500$ at temperatures $T = 300$ K (open triangles) and $T = 240$ K (open square). The fits (bold lines) are done with a power law $At^{-\mu}$. $A = 0.059$, $\mu = 1.50 \pm 0.05$ at $T = 300$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

In figures 5 and 6 we report the residence time distributions (RTD) $\psi(t)$ at the highest $T = 300$ K and the lowest $T = 240$ K temperatures investigated for $N_{\mathrm{W}} = 1000$ and 1500. The RTD, calculated for the molecules in the layer 14 Å $< R <$ 20 Å, shows the predicted power law behaviour of equation (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 RTs of the molecules has been observed in computer simulation and experiments on water in contact with proteins [5]. They are specifically related to the interaction of the solvent with the protein sites.

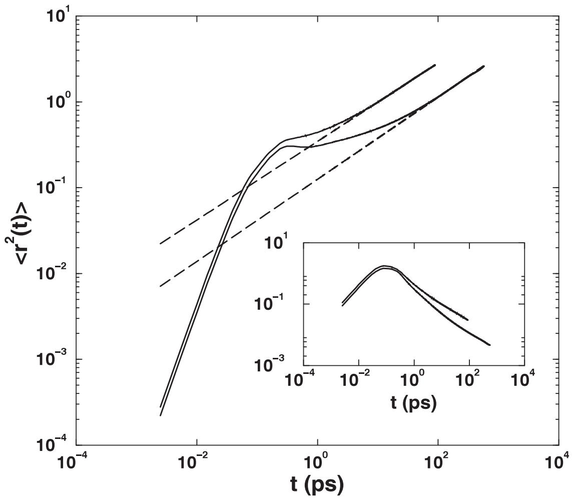

Figure 7. MSD of water molecules in the layer 14 Å $< R <$ 20 Å for $N_W = 1000$ at temperatures $T = 300$ and 240 K from the top. The long dashed lines are the fits to a sublinear behaviour $\langle r^2 \rangle \propto t^\alpha$ with $\alpha = 0.46 \pm 0.05$ at $T = 300$ K and $\alpha = 0.48 \pm 0.05$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

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 ångström shells close to protein hydration sites [5]. 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 μ at $N_W = 1500$ and ambient temperature is slightly different from the preliminary one reported in [13], where the statistics were poorer.

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

$$\langle r^2(t) \rangle \propto t^{\mu - 1}. \tag{3}$$

From the fit of the long time behaviour of the MSD for $N_W = 1000$ and 1500, reported in figures 7 and 8, we get the values of the exponent μ which are consistent with the exponents obtained from the power law behaviour of the RTD seen in figures 5 and 6.

In the lower hydration case $N_W = 500$, figure 9, the RTD decays for a long time with an exponent similar to the previous cases, $\mu = 1.45 \pm 0.05$ and 1.55 ± 0.05 for $T = 300$ and 240 K respectively, but the MSD shows, as seen in the inset of figure 9, a long time behaviour not in agreement with the one predicted by equation (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.

4. 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 the low hydration regimes, where the larger amount of water resides in the shells closer to the hydrophilic surface. We found drastic changes to the diffusion of the water molecules.

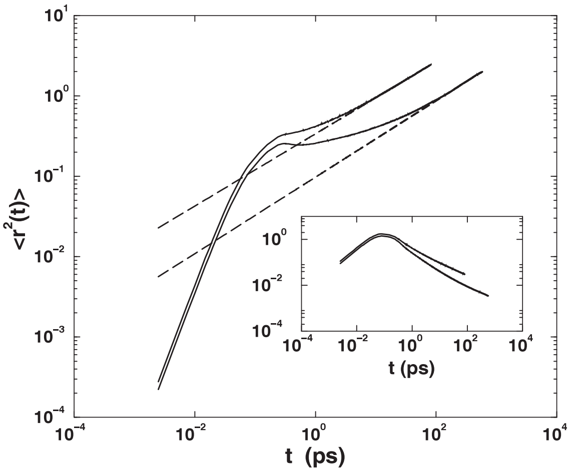

Figure 8. MSD of water molecules in the layer 14 Å $< R <$ 20 Å for $N_W = 1500$ at temperatures $T = 300$ and 240 K from the top. The long dashed lines are the fits to a sublinear behaviour $\langle r^2 \rangle \propto t^\alpha$ with $\alpha = 0.45 \pm 0.05$ at $T = 300$ K and $\alpha = 0.48 \pm 0.05$ at $T = 240$ K. In the inset are reported the functions $\langle r^2 \rangle / t$.

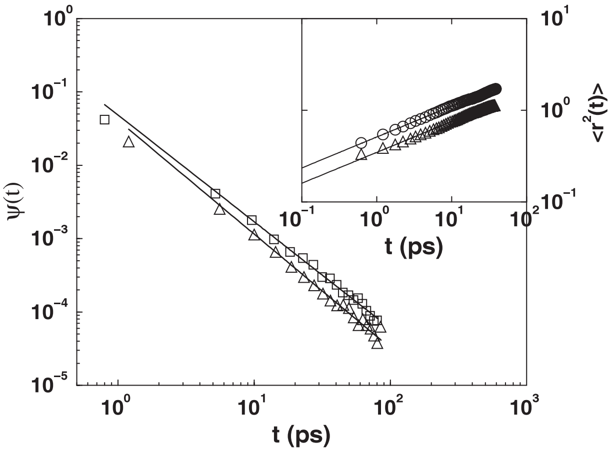

Figure 9. Main figure: log–log plot of the RTD of the water molecules in the layer 14 Å $<$ $R <$ 20 Å for $N_W = 500$ at temperatures $T = 300$ K (open squares) and $T = 240$ K (open triangles). The fit (bold lines) is done with a power law $At^{-\mu}$, with $A = 0.048$, $\mu = 1.45 \pm 0.05$ for $T = 300$ K and $A = 0.041$, $\mu = 1.55 \pm 0.05$ for $T = 240$ K. Inset: MSD of water molecules in the layer 14 Å $< R <$ 20 Å for $N_W = 500$ at temperatures $T = 300$ and 240 K. The bold line is the fit to a sublinear behaviour $\langle r^2 \rangle \propto t^\alpha$ with $\alpha = 0.34 \pm 0.05$ for both $T = 300$ and 240 K.

From a layer analysis for the investigated hydrations we find that the diffusive regime of the molecules being close to the substrate over a long period is characterized by a sublinear trend. This trend is very different with respect to the one found at higher hydrations for the water molecules which are at least 4 Å from the surface [10, 11]. In that case in the long time limit the MSD grows linearly.

The sublinear behaviour found here is a process of anomalous diffusion, a class of phenomena which has attracted the attention of investigators for a long time [19]. The anomalous diffusion has usually to deal with particles in contact with substrates. A typical phenomenon is the dynamics of adsorbed molecules [18]. The anomalous diffusion has been shown to be generated by a distribution of waiting times which decay for a long time with a power law behaviour. So 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 sites of the substrate modulate the RT of the molecules. Particularly interesting is the case of water molecules in contact with proteins [5]. In our case, where the system is in contact with a rigid and disordered substrate, the dispersive transport regime shows up in the power law decay of the RTD with an exponent which also determines the long time tail of the MSD. In our system the exponent of the long time behaviour of the MSD is related to the long time decay of the RTD of the molecules in the same layer for the cases $N_\mathrm{W} = 1500$ and 1000, as theoretically predicted [5].

For the lowest hydration case ($N_\mathrm{W} = 500$) 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, observed in the snapshots of the confined water configurations [15], 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.

Acknowledgment

We thank J Baschnagel for useful and stimulating discussions.

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