Double dynamical regime of confined water

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The Van Hove self correlation function of water confined in a silica pore is calculated from Molecular Dynamics trajectories upon supercooling. At long time in the α relaxation region we found that the behaviour of the real space time dependent correlators can be decomposed in a very slow, almost frozen, dynamics due to the bound water close to the substrate and a faster dynamics of the free water which resides far from the confining surface. For free water we confirm the evidences of an approach to a crossover mode coupling transition, previously found in Q space. In the short time region we found that the two dynamical regimes are overimposed and cannot be distinguished. This shows that the interplay between the slower and the faster dynamics emerges in going from early times to the α relaxation region, where a layer analysis of the dynamical properties can be performed.

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I. INTRODUCTION

The behavior of water below its freezing point upon supercooling is not easily investigated by experimentals since nucleation processes drive the liquid toward its crystalline phase. This phenomenon prevents the observation of the transition of the supercooled liquid to the glassy phase. Molecular dynamics simulations predict a dynamical transition in the supercooled region well described by Mode Coupling Theory (MCT). In the idealized version of MCT the liquid undergoes a structural arrest at a temperature $T_C$. This temperature in real liquids coincides with the cross over temperature at which the structural relaxations of the supercooled liquid are frozen. In most liquids hopping processes start occurring close to and below $T_C$ and these processes ensure ergodicity to the system in this region. When also hopping is frozen the thermodynamic glass transition takes place. Ideal predictions of MCT are well tested on approaching $T_C$ in the region where hopping processes are negligible.

Increasing interest in the study of water when confined arises mainly because modifications of the behavior of this liquid with respect to the bulk phase are closely connected to technological and biophysical problems. In particular water seems to be more easily supercooled when confined. This might open an experimental window in a region of the phase diagram that is experimentally not accessible for the bulk.

Both simulations and theoretical modelizations of water confined between two parallel hydrophobic walls predict new scenarios for thermodynamics and phase behavior. Recent experiments on water confined between two slits of mica found that hydrophilic confinement seems to primarily suppress the hydrogen bond network associated with the freezing. Similar results have been found in the case of a two dimensional confinement in vermiculite clay and in molecular dynamics of water in spherical cavities. A slow relaxation was found for water close to the surface of protein. It has also been observed more specifically in the region around freezing that in water confined in different environments the molecules close to the substrate behave differently with respect to the molecules in the middle of the pores. The term of bound water as distinct from free water has been introduced in order to distinguish the portion of water which resides in layers close to the substrate and does not show a real freezing transition, from the water far from the surface which behaves more similarly to the bulk water.

Recent neutron diffraction experimental studies on water confined in the hydrophilic nanopores of Vycor glass have also evidenced a severe distortion of the hydrogen bond network. The slow, α, relaxation typical of glass formers has been clearly observed on water confined in Vycor upon supercooling by means of both a very refined spin-echo technique and a quasi elastic neutron scattering experiment. Evidence of low frequency scattering excess typical of strong glass formers has been also observed on the same system for low hydration levels of the pore.

We have conducted computer simulation work on a model for water confined in Vycor, where we found that microscopic forces due to an hydrophilic surface can induce a layering effect in water with the formation of a double layer structure close to the surface.

In our previous works on dynamics we concentrated mainly on the study of the molecules which reside on the average far from the solid surface identified as the free water, in particular we studied the intermediate scattering function in the α-relaxation region. MCT appears to work well in its idealized form for free water. We were able to estimate the cross-over temperatures and other MCT parameters for the full hydration and for the half hydration cases.

In this paper we present results obtained from Molecular Dynamics (MD) simulation at full hydration which show a clear evidence that our way of separating water
molecules in two sets, namely the very slow bound water that resides in the first two layers close to the substrate and the faster free water in the inner part of the pore is unique for our system, but only in the time window of the α-relaxation. This effect is in fact clearly visible in the Van Hove self correlation function of the confined water $G_S(r,t)$, presented here for the full hydration of the pore.

In the next section after introducing the Van Hove self correlation function we show its behavior in supercooled bulk water for a comparison with the confined case. In Sec. III we give some details about our simulation of confined water and show the layering effect which takes place in our system. In Sec. IV we present and discuss the results obtained for the Van Hove self correlation functions of the confined water. The final section is devoted to the conclusions.

II. THE VAN HOVE SELF CORRELATION FUNCTION OF BULK WATER

The Van Hove self correlation function (VHSCF) is defined for a system of $N$ particles or molecules as

$$G_S(r,t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \delta \left[ \mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t) \right] \right\rangle$$

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which can be measured in an incoherent quasielastic neutron scattering experiment.

The functions (1) and (2) contain the information which concerns the single particle dynamics and can be directly evaluated from MD trajectories. Even if they are equivalent while (2) would allow a more direct comparison with experiments, when available, the function (1) gives a more detailed and intuitive description of the motion of the particle in the fluid.

We now discuss the behavior of VHSCF for water in its bulk supercooled phase for a comparison with the confined case. We conducted MD simulations in the NVE ensemble with 216 water molecules. The model potential used is the SPC/E. This potential, at variance with ST2, shows a glassy MCT behavior upon supercooling. We cooled the system along the 0 MPa isobar characterized by a $T_C$ estimated to be 194 K. In order to equilibrate the system at such a supercooled temperature a run of 100 ns was performed with a timestep of 0.2 fs.

In Fig. 1 we show $4\pi r^2G_S(r,t)$ of the oxygens as function of $r$ at different times. We can clearly distinguish different time regimes mastered by the caging occurring in supercooled liquids. Looking at the SISF in the inset we see that for short times ($t < 0.04$ ps) the system is in the ballistic region, the corresponding $4\pi r^2G_S(r,t)$ shows a sharp peak and decays rapidly to
zero. For intermediate times (0.2 < t < 100 ps) the system is in the β relaxation region, well described by the MCT, and the “cage effect”, evidenced by the clustering of $4\pi r^2 G_S(r,t)$, is rather marked as we are right on the estimated MCT crossover temperature. This temporal region corresponds to the plateau of the SISF. Finally in late the α-relaxation region, where the SISF is described by a stretched exponential decay, the system is entering the diffusive regime and long tails develop in the $4\pi r^2 G_S(r,t)$ which extends to longer distances at increasing time. This behaviour of the VHSCF of supercooled water is shared by most liquids approaching the MCT crossover temperature $T_C$.

III. LAYERING EFFECTS IN CONFINED WATER

We describe in this section our confined system and briefly summarize the main results of the single particle analysis conducted in the Q,t space. We performed MD simulations of SPC/E water in a cylindrical pore of 40 Å diameter and 71.29 Å height. The pore is carved in a simulated silica glass. As described in details in previous works, the surface of the pore is treated in order to reproduce the main average properties of the pores of Vycor glass. The substrate results to be a corrugated surface composed by silicon atoms, bridging oxygens bound to silicons and non-bridging oxygens saturated with acidic hydrogens. Different Coulomb charges are attributed to the sites of the surface representing the four types of atoms, moreover the oxygen sites interact with the oxygen sites of the water by means of a Lennard-Jones potential. We analyze in the following the full hydration case which corresponds to 2600 molecules. The pore surface results to be strongly hydrophilic, as can be seen from the density profile shown in Fig. 2. A double layer of water molecules is clearly seen close to the surface of the Vycor in the region between 15 and 20 Å, where the pore surface is located. Moving toward the center of the pore the density reaches a value close to 11% of the

FIG. 3: In the main frame the total VHSCF for the oxygens of the water molecules for $T=298$ K and $t=1$ ps (lower curve) and $T=210$ K and $t=25.6$ ps. In the inset the corresponding total SISF (lower T on the top). The arrows mark the times in the α-relaxation region at which the VHSCF are evaluated.

FIG. 4: In the main frame layer analysis of the VHSCF for the oxygens of the water molecules at $T=298$ K and $t=1$ ps. The total correlator (dashed line) also displayed in Fig. 1 is shown together with the contribution coming only from oxygens that move in the inner part of the pore (continuous line) i.e. of the free water and with the contribution coming from the first two layers close to the substrate (long dashed line) i.e. of the bound water. In the inset the corresponding layer analysis for the SISF (lines as in the main frame). The arrows mark the time at which the VHSCF are evaluated.

FIG. 5: In the main frame layer analysis of the VHSCF for the oxygens of the water molecules at $T=210$ K and $t=25.6$ ps. In the inset the corresponding layer analysis for the SISF. The arrows indicate the times at which the VHSCF is evaluated.
IV. THE VAN HOVE SELF CORRELATION FUNCTION OF CONFINED WATER

We now move to the description of the dynamics of confined water upon supercooling through the analysis of the VHSCF.

In Fig. 6, we show the angular average of the VHSCF as defined in Eq. \( \langle \mathbf{G}_S(r,t) \rangle \), of the oxygens of the water molecules confined in Vycor at \( T = 298 \) K and \( T = 210 \) K. For the sake of clarity only the highest and the lowest temperatures investigated are shown in the pictures since the intermediate curves display a continuous trend. The curves have been calculated for times corresponding to the late \( \alpha \) region as best shown in the inset where the corresponding SISF are plotted. The more striking feature of the VHSCF is the presence in both curves of a double peak structure. A first sharper peak, located at short distance, is followed by a second broader peak.

By considering the radial density profile of Fig. 2, analogously to what done for the SISF in previous work\(^{16,17,20}\), we separated also for the VHSCF the contribution of the molecules in the outer double layer close to the surface of the cylindrical pore between 15 Å and 20 Å from the contribution of the remaining molecules between the center of the pore and 15 Å. The calculation is explicitly performed for a selected region by considering as contribution to Eq. \( 1 \) only water molecules that at time \( t = 0 \) are inside the considered region until they remain in that region.

In Fig. 7, we report the inner layer (free water) contribution and the outer layer (bound water) contribution to the total VHSCF of Fig. 6 at \( T = 298 \) K. In the inset we show the same layer analysis performed for the intermediate scattering function \( 2 \) of the confined water. We note that the two VHSCF are singly peaked in the \( \alpha \)-relaxation region and that each peak corresponds to one of the two peaks of the total VHSCF. The VHSCF of the bound water is localized and decays to zero in few Å, while in the free water the molecules are more distributed in space and the corresponding VHSCF decays slowly.

In Fig. 8, the same analysis is shown for \( T = 210 \) K. Features are similar to the previous figure. Interestingly, this division in two subset reveals to be temperature independent in our system and therefore a general characteristic in the range of temperatures investigated for this time region.

The VHSCF at 210 K for 25.6 ps is more localized close to the origin with respect to the corresponding correlator calculated at room temperature for 1 ps, as shown in Fig. 6. This is due to the slowing down of the dynamics as the temperature is decreased to the region of the supercooled liquid.

The contribution due to the molecules which reside closer to the substrate (bound water) is reported separately in Fig. 7. It is evident that, at variance with the free water, the bound water suffers a severe slowing down
FIG. 7: In the main frame VHSCF of bound water for $T=298$K at $t=1$ps (curve on the right) and $T=210$K at $t=25.6$ ps. In the inset the corresponding SISF (lower temperature on the top). The arrows indicate the times at which the VHSCF is evaluated.

FIG. 8: VHSCF of bound water for $T=210$K at $t=25.6$ ps (thick line) compared with VHSCF of bulk water for $T=190$K at $t=1$ ps (thin line). A fit to a Gaussian is superposed to the VHSCF of the bulk (long dashed thick line).

FIG. 9: In the main frame total VHSCF for $T=298$ K (dashed line) and $T=210$K (continuous line) both at $t=0.08$ ps. In the inset the corresponding SISF (lower temperature on the top). The arrow marks the time at which the VHSCF are evaluated.

of the dynamics already at room temperature. The two distributions of distances corresponding to $T=298$K and $T=210$ K appear in fact not to differ substantially from each other.

The comparison of the VHSCF of supercooled bound water calculated in the $\alpha$ region with the VHSCF of bulk water (see Fig. 1) shows that the molecules are much less mobile in confined bound water. This is best seen in Fig. 5 where we report the VHSCF of confined water at $T=210$ K in the $\alpha$-relaxation region with the most similar VHSCF of bulk water at $T=190$ K, namely the one in the intermediate region of the rattling in the cage. We note that in spite of the fact that the curves are calculated in two different dynamical regimes they are very similar. Therefore the confined VHSCF reproduces the features of molecules that can move essentially in the cage of the nearest neighbors. The peak of the VHSCF curve of confined bound water is shifted left, due to higher density of bound water with respect to the bulk. It also displays a much longer tail.

In Fig. 9 we report the total correlator calculated for the highest and the lowest temperature investigated in the early times. At a first glance the behavior might seem quite similar to the late $\alpha$ one. Nonetheless it turned out that the shell analysis is not valid in this region. We therefore conclude that our layer analysis is limited to the temporal range of the $\alpha$-relaxation for this model while for early times the two dynamical regimes cannot be distinguished.

V. SUMMARY AND CONCLUSIONS

We presented a study of the single particle Van Hove correlation function for a model of water confined in a silica pore of Vycor glass.

The separation in two well distinct subsets of water molecules in the hydrophilic pore hypotized in a previous analysis is confirmed as unique. The VHSCF is in fact doubly peaked at all temperatures and a layer analysis of the correlators shows that water close to the substrate, bound water, contributes only to the first peak while free
water contributes only to the second peak. This separation is however valid only in the slow relaxation region commonly named as $\alpha$. No separation of dynamical regimes has been found in the fast relaxation region.

Due to the strong resemblance that we found in bound water with respect to water confined in biological environments we infer that the double dynamical behavior of this system is shared by water confined in biological environments like surrounding proteins.

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