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Water confined in MCM-41: a mode coupling theory analysis

P Gallo¹, M Rovere¹ and S-H Chen²

¹ Dipartimento di Fisica, Università 'Roma Tre', Via della Vasca Navale 84, 00146 Roma, Italy

² Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

E-mail: gallop@fis.uniroma3.it

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Abstract

In this paper we analyze molecular dynamics simulation results on supercooled water in a MCM-41 pore in order to test the mode coupling theory. A layer analysis must be performed for water in the pore in order to exclude the contribution of water bound to the strongly hydrophilic surface. Upon supercooling a range of temperatures is reached where the liquid follows the mode coupling theory. From the power law behavior of the relaxation times extracted from the Kohlrausch–William–Watts fit to the self-intermediate scattering function, we obtain the crossover temperature T_C and the γ exponent of the theory. The time–temperature superposition principle is also satisfied. A fit to the von Schweidler law yields a coefficient b from which all the other parameters of the theory have been calculated. In particular, we obtained the same value of γ as extracted from the power law fit to the relaxation times, in agreement with the requirements of the theory. For very low temperatures, the mode coupling theory no longer holds as hopping processes intervene and water turns its behavior to that of a strong liquid.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the last few years an intense debate has been developing about glass transition in confinement. This issue is of great interest in biology, geophysics, and for technological applications where confined fluids often play fundamental roles [1, 2]. In this context dynamic crossover phenomena observed in bulk and confined liquids in the supercooled region are of particular relevance [3–10].

In the region of mild supercooling it has been shown that the mode coupling theory, MCT, of the evolution of glassy dynamics [11], works well also for liquids in several kinds of confinement [12–18]. The MCT is able to describe the dynamics of bulk liquids in the supercooled region on approaching a crossover temperature T_C . Above T_C ergodicity is attained through structural relaxations while below this temperature structural relaxations are frozen and only activated processes permit the exploration of the configurational space. When also hopping is frozen the system reaches the temperature of glass transition. Above T_C the relaxation mechanism of the supercooled liquid can be described as mastered by the cage effect. Nearest neighbors

surround and trap the tagged particle forming a cage around it. When the cage relaxes, due to cooperative motions, the particle diffuses. The MCT describes the dynamics for the density correlator introducing a retarded memory function. In the idealized version of the MCT, hopping processes are neglected and the nonlinear set of integro-differential equations can be solved analytically to the leading order in $\epsilon = (T - T_C)/T_C$, the small parameter of the theory, deriving universal results for the behavior of the density correlator. Within these approximations T_C is the temperature of structural arrest of the ideal system. The success of this theory is due to the fact that on approaching T_C from above the predictions of the idealized version of the MCT are verified in experiments and computer simulations. In many systems hopping starts to appear above and close to T_C , introducing deviations from the idealized behavior.

The exploration of the deep supercooled region of water is experimentally hampered by homogeneous nucleation [19, 20], although the possibility of reaching the glassy state from high temperatures it is not forbidden [21]. Molecular dynamics (MD) simulations of bulk water have indicated that water behaves *à la mode* coupling upon supercooling [22–24]. Experimental and theoretical studies of water in a Vycor

pore have indicated that MCT holds also for water in mild confinement [12, 13, 25, 26] where the temperature of maximum density of water also exists [27].

In recent studies on water in MCM-41 a transition was observed from a fragile to a strong (FTS) behavior of the liquid [3, 7, 28]. In our previous study with MD on SPC/E water confined in MCM-41 we successfully succeeded in reproducing experimental findings by performing a phenomenological analysis [5].

Following the MCT description of the glassy dynamics the FTS transition is a crossover from the region mastered by the cage effect to the region mastered by hopping. In this respect, we test in this paper whether the dynamics of confined water approaching the FTS transition verifies the MCT predictions coming from the asymptotic expansion near the crossover temperature.

The paper is structured as follows: in section 2 we describe the simulation details. Section 3 is devoted to the MCT study of the α -relaxation region, section 4 deals with the test of the MCT time–temperature superposition principle (TTSP). Section 5 is devoted to conclusions.

2. Computer simulation of confined water

MCM-41 is a silica porous material and is one of the most used mesoporous substrates for studying confined fluids, since it is very well characterized with pores periodically arranged in space [29]. Different MCM-41 samples are used in experiments, characterized by the different procedures involved in obtaining the final configuration of the material. In our simulations we study water molecules confined in a single pore modeled to mimic the main features of the real system.

The cylindrical pore of 15 Å in diameter is carved in a cubic box of silica of length $L = 42.78$ Å. The silica glass is obtained from MD simulation performed at constant volume starting from a β -cristobalite crystal, with the Vessal *et al* potential [30]. The MD is performed at constant volume.

In the final configuration at the surface of the pore there are bridging oxygens (bOs) with two silicon neighbors and non-bridging oxygens (nOs) with only one silicon neighbor. The nOs were saturated with acidic hydrogens (aHs). The axis of the cylindrical pore is assumed to be along the z -direction.

The water molecules are inserted in the center of the pore in a starting lattice configuration. The water is modeled with the SPC/E three site potential, where one site (Ow) represents the oxygen and the other two (Hw) the hydrogens. The interaction of the water sites (Ow, Hw) with the atoms of the substrate (Si, bO, nO, aH) is determined by an effective potential already used in previous simulations [31]. Periodic boundary conditions are applied to the cubic box.

The shifted force method was adopted with a cut-off at 9 Å for all the interactions since long runs of simulation are needed for the study of dynamical properties in regions where systems approach the glass transition. The choice of the size of the cubic box length was done by taking into account the cut-off of the potentials and the minimum image convention.

The temperature is kept under control during the equilibration by means of the Berendsen thermostat. Production runs

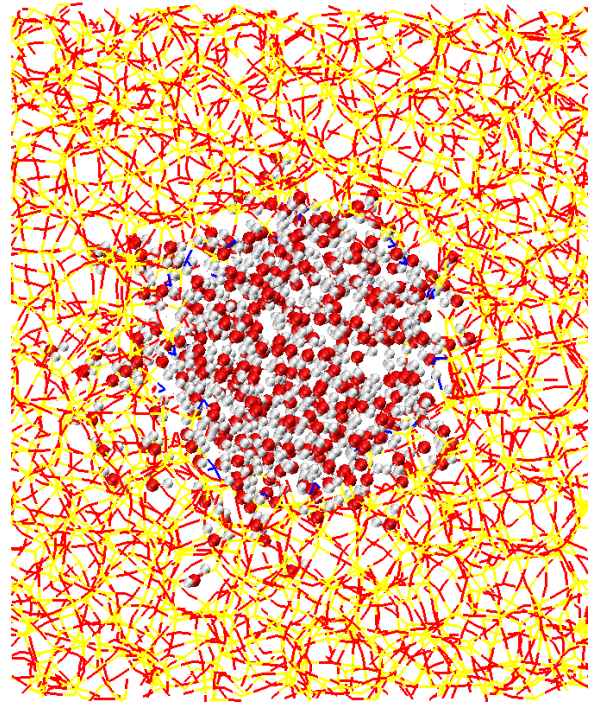


Figure 1. Two-dimensional projection of a snapshot of water contained in a pore of MCM-41 at $T = 300$ K. The box length is $L = 42.78$ Å and the diameter of the cylindrical pore is 15 Å. We can distinguish in the picture the acidic hydrogen (inner, darker sticks), the water molecules (dark and light spheres), and the silica molecules (outer sticks).

are done in the microcanonical ensemble with a time step of 1 fs. In this paper we report results obtained with a number of water molecules $N_w = 380$. The number was tuned to get an average density around 1 g cm^{-3} in the inner part of the pore. We simulated temperatures ranging from $T = 300$ to 190 K. For each temperature equilibration runs between 5 ns at high T and 12 ns at low T are performed. The self-intermediate scattering functions (SISFs) are calculated from a number of equilibrated configurations ranging from 10 ns at high T to 20 ns at low T .

A snapshot of the system described is reported in figure 1 for $T = 300$ K.

3. MCT dynamics: the α -relaxation region

Structural relaxation and slowing down of the dynamics close to the MCT crossover temperature T_C can be conveniently characterized by analyzing the SISF

$$F_{(s)}(Q, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \exp(-i\mathbf{Q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]) \right\rangle. \quad (1)$$

The time dependence of this correlation function is analyzed as a function of temperature for the wavevector $Q = Q_0$ corresponding to the position of the main peak of the static structure factor where MCT caging is best evident.

According to MCT prediction upon supercooling in the limit of long time the SISF enters in the α -relaxation

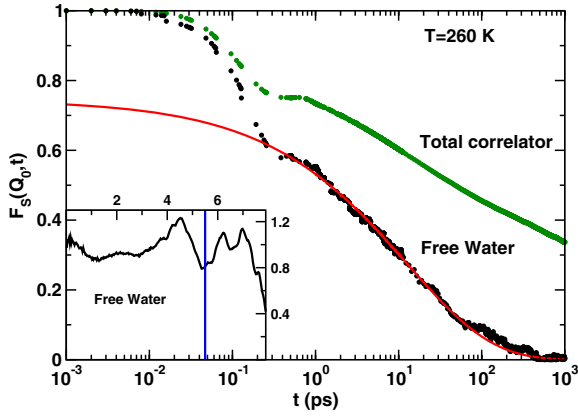


Figure 2. Inset: density profile of water inside the MCM-42 pore. The vertical line delimitates the free water region. Main frame: SISF calculated for water oxygens at the peak of the structure factor $Q_0 = 2.25 \text{ \AA}^{-1}$ at $T = 260 \text{ K}$. The upper curve is the correlator calculated from all water molecules. The lower curve is the contribution of the SISF calculated only for the free water molecules. The continuous line is the fit to the KWW stretched exponential function, see equation (2).

regime where its behavior can be fitted with the Kohlrausch–Williams–Watts (KWW) stretched exponential

$$f(t) = f_Q \exp[-(t/\tau_\alpha)^\beta] \quad (2)$$

where β is the Kohlrausch exponent and it must be in the range $0 < \beta < 1$, τ_α is the relaxation time, and f_Q is the non-ergodicity parameter.

In figure 2 we report, as an example, the total SISF correlator calculated for confined water. Although it shows the two-step relaxation scenario typical of glass formers, in a previous study we have already evinced that these long time decays of the correlators cannot be fitted with equation (2) at all temperatures investigated. For water confined in a hydrophilic medium, in fact, the first layer of water molecules which reside close to the surface is very slow even at ambient temperature and it is characterized by a subdiffusive behavior also at long times [32]. This layer 2 Å thick starting from the surface is shown in the lower inset of figure 2. In order to do the KWW fit, we had to perform a layer analysis, taking into account only free water molecules, defined as those molecule that move in the free water region also shown in figure 2. Once the free water correlator is calculated we were able to fit all the temperatures with the KWW. As an example we show in the main frame of figure 2 the SISF at $T = 260 \text{ K}$, where we separated the free water contribution from the total one. From the figure it is evident that the curve for free water fits very well the KWW function and this is true for all temperatures investigated. For further details see [5].

We report in figure 3 the Kohlrausch exponent β and the f_Q extracted from the fit of the SISF to equation (2). We found that the β exponents extracted from the fits are slowly decreasing at high temperatures and reach a plateau value as temperature is lowered. The values of the β exponent in confinement appear lower than the bulk [22, 23] but with a similar trend, see figure 3. Compatible values have been

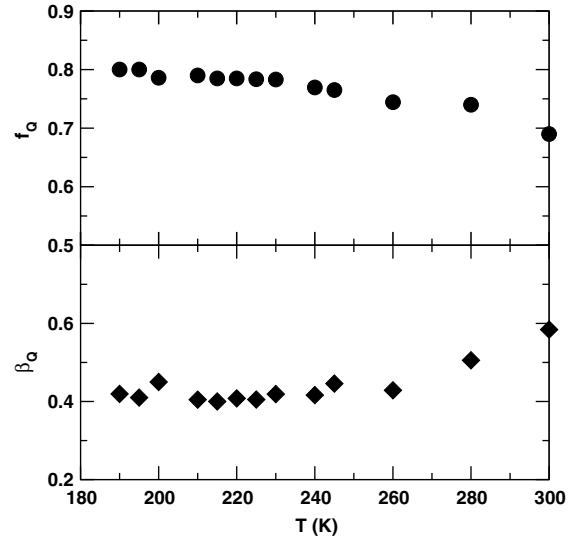


Figure 3. Top frame: non-ergodicity parameter. Bottom frame: Kohlrausch exponent. Both quantities are extracted from the fit of the SISF to equation (2) at different temperatures.

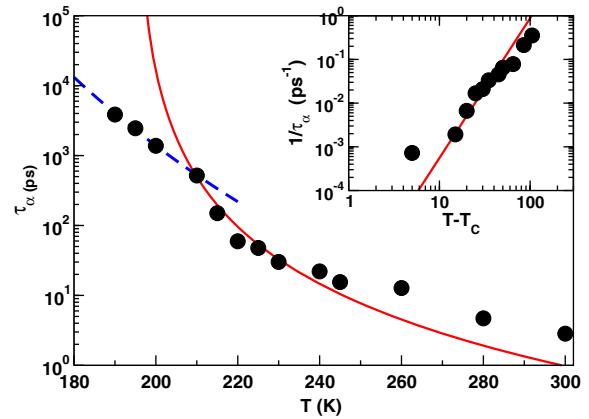


Figure 4. Relaxation time as a function of temperature. Main frame: the continuous line is the fit to the MCT power law behavior, see equation (3). The dashed line is the fit to the Arrhenius behavior. Inset, inverse relaxation time as a function of $(T - T_C)$. The fit is reported as a continuous line. The lowest point reported is the first that deviates from MCT behavior.

obtained from QENS experiments on confined water in MCM-41 [7, 3].

The non-ergodicity parameter f_Q also obtained from the fit of the SISF to equation (2) and shown in figure 3 displays only a weak increasing at higher temperatures and also reaches a plateau.

The most relevant quantity to investigate in order to define the MCT crossover temperature is the relaxation time and its dependence on the temperature. We started our MCT analysis from $T = 240 \text{ K}$ where both β and f_Q reach a plateau. The relaxation time is shown in figure 4 with the fit to the MCT power law predicted behavior

$$\tau_\alpha^{-1} \propto (T - T_C)^\gamma. \quad (3)$$

The values that we obtained from the fit are $T_C = 195 \text{ K}$ and $\gamma = 3.2$, well in the range predicted by MCT, $\gamma > 1.766$.

Hopping coexists with structural relaxations for the lowest temperatures investigated and causes deviation from MCT behavior. By further decreasing the temperature below $T = 210$ K hopping effects induce a crossover from a fragile to a strong behavior of τ_α and the system deviates from the MCT behavior.

In previous work we analyzed the behavior of τ_α to make contact with the experimental results. In analogy with experiments on MCM-41 at high temperature, below 300 K, the points were fitted with the Vogel–Fulker–Tamman (VFT) formula (not shown) $\tau_\alpha = \tau_0^{\text{VFT}} \exp[\frac{BT_0}{T-T_0}]$ where B is the fragility parameter and T_0 is an ideal glass transition temperature. This formula is a phenomenological expression often used to characterize fragile glass formers in an alternative to the MCT power law. The parameters extracted from the fit are $B = 0.25$ and $T_0 = 200$ K. Below $T = 210$ K the fit is done with the Arrhenius function (shown in the picture) $\tau_\alpha = \tau_0^A \exp[E_A/k_B T]$ where E_A is the activation energy. We found from our data an activation energy of $E_A = 34$ kJ mol⁻¹, similar to the bulk [33].

We precisely located the temperature of the crossover from fragile to strong as $T_L = (215 \pm 5)$ K.

4. MCT dynamics: the TTSP test

MCT predicts a TTSP in the asymptotic limit of $T \rightarrow T_C$. The TTSP states that the shape of the correlator curves in the late β -relaxation and early α -relaxation time regimes does not depend on temperature. So the intermediate scattering functions behave as

$$F_{(S)}(Q, t) = \hat{\phi}_Q(t/\tau_\alpha(T)) \quad (4)$$

where τ_α is a time scale associated to the α -relaxation decay of the correlation function and $\hat{\phi}_Q$ is a master function. The master function $\hat{\phi}_Q(t)$, according to MCT, has the functional form of the von Schweidler (VS) law,

$$\hat{\phi}_Q(t) = f_Q^c - h_Q(t/\tau_\alpha)^b, \quad (5)$$

where f_Q^c is the non-ergodicity parameter, h_Q is the amplitude factor, and b is the VS exponent.

We used in the scaling of the SISF the $\tau_\alpha(T)$ obtained via the KWW fits of section 3. In figure 5 we report the SISF at $Q = Q_0$ plotted as a function of $t/\tau_\alpha(T)$. In the figure we included the best fit to the VS law, equation (5).

From the figures it is evident that in the long time scale of the α -relaxation regime the rescaled curves that belong to the region where MCT was verified by the power law fit fall on top of each other, defining a master curve $\hat{\phi}_Q(t)$ with the expected stretched exponential form. The TTSP holds in the β relaxation region, where the master function can be fitted to the VS law. The parameters obtained from the VS fit are $f_Q^c = 0.76$, $h_Q = 0.55$, and $b = 0.4$.

Starting from one parameter extracted from the MD data we can calculate all the relevant MCT parameters through the relations

$$\gamma = \frac{1}{2a} + \frac{1}{2b} \quad (6)$$

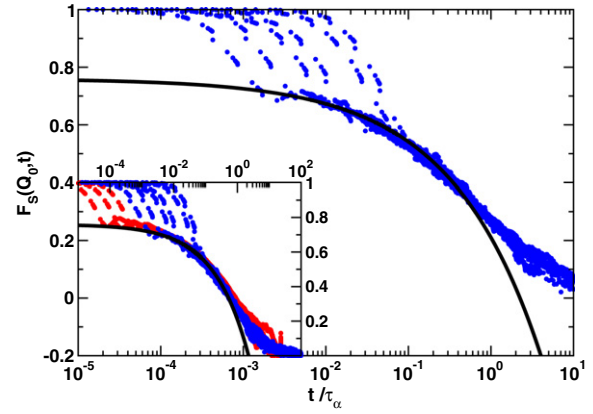


Figure 5. SISF evaluated at $Q = Q_0$ for the temperatures for which MCT holds, scaled by the τ_α obtained from the KWW fit. The continuous line is the fit to the VS law, equation (5). In the inset the same rescaling plot is shown, also including the lowest temperatures, for which MCT does not hold.

$$\lambda = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)} \quad (7)$$

where Γ is the Euler Γ function, a is the critical exponent related to the decay of the correlation functions toward the plateau, and the exponent parameter λ characterizes the system. The parameters must be in the ranges $1/2 < \lambda < 1$, $0 < a < 0.395$, and $0 < b < 1$ [11].

Since we extracted from our analysis both γ from the τ_α and b from the VS, we calculated all the other parameters from b and obtained the γ extracted from the fit of the τ_α . In fact $b = 0.4$ yields $a = 0.25$, $\lambda = 0.85$, and $\gamma = 3.25$ which is practically coincident with the γ extracted from our fit, as expected for consistency with MCT equations.

In the inset of figure 5 we show the master plot including also the three lowest temperature curves, where the system turns to a strong behavior. We observe that the TTSP no longer holds as the curves start to detach from each others.

5. Conclusions

In this paper we focused on the analysis of the relaxation time behavior of water confined in MCM-41 to test MCT in the region of mild supercooling approaching the FTS transition. We have shown that in the range of temperature in which the system shows a fragile behavior MCT is able to describe the dynamics. In particular a power law behavior for the relaxation time holds and $T_C = 195$ K. The TTSP holds and the fit to the VS law gives an exponent b that leads to the same value of γ as the one extracted with the power law. In the fragile region the data could also be fitted with the VFT law. We note that the range of validity of MCT is more limited than the VFT one [5], as it starts from a lower temperature. The last temperature for which both MCT and VFT hold is $T = 210$ K. Below this temperature the system crosses to a strong behavior characterized by hopping.

Acknowledgments

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