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We study by molecular dynamics simulations the dynamical properties of an aqueous solution of NaCl at a concentration of 0.67 mol/kg upon supercooling. In a previous study of the same ionic solution, we have located the liquid-liquid critical point (LLCP) and determined the Widom line connected to the liquid-liquid transition. We present here the results obtained from the study of the self-intermediate scattering function in a large range of temperatures and densities approaching the LLCP. The structural relaxation is in agreement with the mode coupling theory (MCT) in the region of mild supercooling. In the deeper supercooled region the α-relaxation time as function of temperature deviates from the MCT power law prediction showing a crossover from a fragile to a strong behavior. This crossover is found upon crossing the Widom line. The same trend was found in bulk water upon supercooling and it appears almost unchanged by the interaction with ions apart from a shift in the thermodynamic plane toward lower pressures and higher temperatures. These results show that the phenomenology of supercooled water transfers from bulk to solution where the study of the supercooled region is experimentally less difficult. © *2013 AIP Publishing LLC.*
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I. INTRODUCTION

The existence of a liquid-liquid critical point (LLCP) in supercooled water is the topic of a vivid debate in literature. The hypothesis of a LLCP in this liquid was formulated for the first time on the basis of computer simulation of the phase diagram of ST2 supercooled water.[1,2] Several computer simulation studies of different models of water gave support to this hypothesis, see, for instance, Refs. 3–9. This interpretation is based on the polyamorphism of water. When water is vitrified by fast cooling procedures two different coexisting phases of amorphous ice can be obtained. They are called low density amorphous (LDA) and high density amorphous (HDA) ice.[10–14] The hypothesis of the second critical point assumes that at increasing temperature the two amorphous phases evolve into two corresponding metastable phases: the low density liquid (LDL) and the high density liquid (HDL). The LDL-HDL coexistence line would terminate in the LLCP. The presence of a second critical point would also explain the anomalous increases of the thermodynamic response functions of water approaching the singular temperature $T_S = -45\,^\circ\mathrm{C}$ at ambient pressure.[15]

The experimental verification of such a hypothesis is not an easy task, being the approach to the LLCP hampered by homogeneous nucleation. In principle, vitrification can be achieved by a continuous process[16] but experiments have so far not succeeded in passing trough a so called "no-man's land" where only crystalline water can be obtained. Experimental trends found in liquid water in the supercooled region starting from high temperature or in the range just above the glassy states were interpreted in terms of a possible liquid-liquid coexistence terminating in a critical point approximately located at a temperature $T \approx 220$ K and a pressure $P \approx 50$–100 MPa.[17,18] Recent x-ray experiments are also consistent with the LLCP hypothesis.[19–21]

In the last few years the possibility of applying more refined computer simulation techniques, due to the improvement of computer resources, increased the interest and the debate on the issue.[22–34]

Besides the thermodynamic behavior supercooled water shows dynamical properties of great interest upon supercooling. By molecular dynamics (MD) simulations of SPC/E water[35,36] it was found that the relaxation of the density correlator can be interpreted in terms of the Mode Coupling Theory (MCT) of glassy dynamics.[37] Later it was found that this dynamical picture can be transferred in confined water upon cooling.[38,39]

More recently we have shown that in bulk TIP4P water in a large range of temperatures and densities the structural relaxation in the region of mild supercooling is also in agreement with the predictions of the MCT.[40] Besides in the deeper supercooled region we observed a transition from a fragile to a strong behavior of the relaxation time. The fragile to strong crossover (FSC) has been observed in computer simulations of water[6,24,41–43] and in several systems characterized by the formation of tetrahedral networks.[44,45] In water the presence of a FSC is of great relevance in connection with the debate about the LLCP discussed above. In simulations

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of supercooled water it was found that the FSC takes place when the system crosses the so called Widom line (WL).[6,24] The WL is in general defined as the locus where the maxima of the response functions converge in approaching the critical point from the single phase region.[46–49] In supercooled TIP4P bulk water we also observed the coincidence of the FSC with the WL in the single phase region on approaching the LLCP.[40]

Due to the difficulties in performing experiments on pure water in the supercooled region different routes have been explored. In confinement water can be more easily supercooled and studied in region of phase space where crystallization of bulk water cannot be avoided. In fact, the FSC was determined for confined water both in experiments[50–56] and in simulations.[57–59]

Also solutions can represent a viable route to study the supercooled region of water.[21,60–65] The existence of a FSC in concentrated solutions of methanol and of LiCl has been recently found[66–68] with ultrafast femtosecond optical Kerr effect (OKE) spectroscopy, nuclear magnetic resonance (NMR) diffusion measurements, Fourier-transform infrared (FTIR) measurements, and temperature-dependent rheology although different techniques, namely, broadband dielectric and light scattering spectroscopy in a broad frequency range experiments on water and LiCl(aq) do not find it.[69] The difference among the probes must, however, be considered while analyzing different kinds of relaxation times.

The behavior of ionic aqueous solutions upon supercooling is important also in connection to thermodynamics of water since the mixture critical point for a dilute composition will be close to that of the majority component, and its vicinity will indeed be characterized by large density and energy fluctuations. It has recently been shown that the LLCP phenomenon persists for concentrations from low to moderate and importantly that the position of the LLCP of supercooled water in a NaCl(aq) solution is shifted in a portion of phase diagram that can be reached in experiments for certain concentration of salts.[7,70–73]

As a consequence, it is of great relevance to study how the dynamical behavior of water is changed by the presence of ions in mildly concentrated solution.

In our previous work, we determined by MD the phase diagram of the aqueous solution of NaCl at the concentration of 0.67 mol/kg[7] with the potential described in Sec. II. From those calculations, it was possible to approximately locate the position of the mixture LLCP and to derive the WL. In this work, we study the dynamics of the same solution on approaching the LLCP. We test the MCT and search for a possible FSC in order to determine to what extent the interaction with the ions changes the dynamics of water upon supercooling.

In Sec. II, we describe our simulation method and the force field used in our calculations. In Sec. III, we show the phase diagram of the solution with the LLCP and its WL. In Sec. IV, we present the study of the self-intermediate scattering functions (SISF) upon supercooling along isochores and determine the behavior of the relaxation time with evidences of FSC in a range of densities. In Sec. V, we connect the FSC to the behavior of the WL. Section VI is devoted to conclusions.

II. MODEL AND SIMULATION METHODS

We studied by MD simulation TIP4P water in solution with NaCl at the concentration of $c = 0.67$ mol/kg. In the TIP4P model,[74] water is represented as a rigid molecule with four sites. The sites of the hydrogen atoms (H) bear a positive charge of $0.52e$ and are connected to the oxygen (O) site. The O–H distance is 0.9572 Å and the H–O–H angle measures 104.52°. The O site is assumed to be neutral and the negative effective charge is attributed to a fourth site (M) slightly shifted by 0.15 Å from the O in the molecular plane along the H–O–H bisector. The negative charge of the M site neutralizes the hydrogen charges. The oxygens of the water molecules interact with a Lennard-Jones (LJ) potential. It is well known that the TIP4P model can reproduce well both structural and thermodynamic properties of water.[7,75] In our simulations also the ion-ion and the ion-water interactions are represented by a combination of Coulombic and LJ potentials

$$u_{\alpha\beta}(r) = \frac{q_\alpha q_\beta}{r_{\alpha\beta}} + 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^6\right], \quad (1)$$

where the ion-ion parameters are taken from Jensen and Jorgensen (JJ)[76] and the ion-water parameters are calculated with geometric mixing rules. The parameters in Eq. (1) are reported in Table I.

The simulations were performed with fixed number of $N_w = 500$ water molecules, 6 cations, and 6 anions corresponding to a concentration of $c = 0.67$ mol/kg.

We applied periodic boundary conditions. The interaction potentials were truncated at $r_{cut} = 9$ Å taking into account the long range electrostatic effects with the Particle Mesh Ewald (PME) method.

We focused on the calculation of the the self-intermediate scattering functions (SISFs) in a range of densities from $\rho = 0.95$ g/cm³ to 1.10 g/cm³ and temperatures from $T = 300$ K down to 190 K. As explained in Sec. III our previous work indicates in this portion of the thermodynamic $\rho - T$ plane the presence of the WL. We performed MD simulations with the use of the Berendsen thermostat[77] to thermalize the system at each temperature. After equilibration the production runs were performed in the microcanonical ensemble, in a range from 0.1 ns at the highest temperatures up to 50 ns at the lowest ones. The simulations were performed using partially the DLPOLY[78] package and partially the GROMACS[79,80] package, both packages in the parallel version.

TABLE I. Lennard-Jones parameters of the interactions between oxygen atoms in the TIP4P water molecule and between ions. Mixed interactions are obtained with geometric mixing rules. H and M sites of water interact only by Coulomb potential.

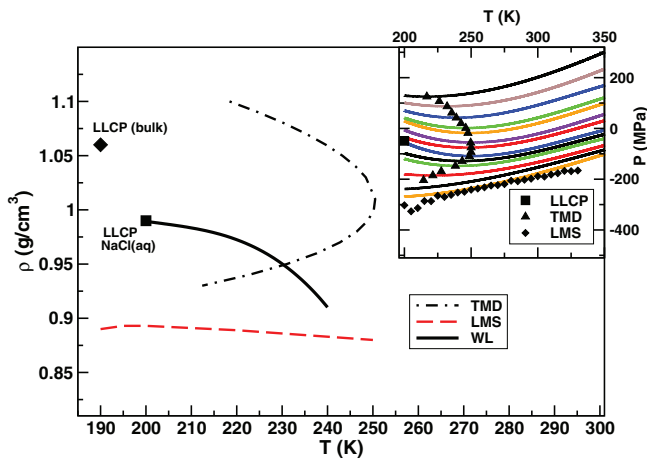|	ϵ (kJ/mol)	σ (Å)
O–O	0.649	3.154
Na–Na	0.002	4.070
Cl–Cl	2.971	4.020

FIG. 1. Phase diagram of the NaCl solution with TIP4P water as adapted from Ref. 7. Main panel: in the $\rho - T$ plane is reported the temperature of maximum density (TMD) (dotted dashed line); the limit of mechanical stability (LMS) (dashed line); the Widom line (WL) defined in the text (bold line); the estimated location of the liquid-liquid critical point (LLCP) for this solution (full square); the LLCP of the pure TIP4P for comparison (full diamond). Inset: isochores of the solution in the range of densities from the top $\rho = 1.10$ g/cm^3 to the bottom $\rho = 0.90$ g/cm^3; the TMD and the LLCP are also reported (for details see Ref. 7).

III. WIDOM LINE OF THE IONIC SOLUTION

In Fig. 1, we report the results obtained in our previous simulations.[7] In the main panel in the $\rho - T$ plane the broken line represents the line of mechanical stability (LMS) of the liquid defined by the condition $(\partial P/\partial \rho)_T = 0$. This line is obtained locating the minima along each isotherm. In the figure, we also report the line of the temperature of maximum density (TMD). In the inset, where some of the isochores studied are reported in the $P - T$ plane, the TMD is individuated by the minima found along each isochore.

From the analysis of the behavior of the isochores, the convergence of the lines of maxima of the isothermal compressibility K_T and of the constant volume specific heat C_V it was possible to estimate the position of the critical point of the transition from the low to the high density liquid phase of water in solution. In Fig. 1, the LLCP of the solution ($T_c = 200$ K, $P_c = -50$ MPa, $\rho_c = 0.99$ g/cm^3) is shown both in the $\rho - T$ and in the $P - T$ planes. In the main panel of the figure we also report the position of the LLCP for the bulk phase of TIP4P water. The LLCP of the aqueous solution is shifted at lower density and higher temperature with respect to the LLCP estimated for the TIP4P water.

By moving from the LLCP into the single phase region, the WL was located with the same procedure used for TIP4P pure water, namely, from the maxima of the constant volume specific heat C_V. Close enough to the LLCP we expect all the response function maxima to converge into the WL. And in fact, as in bulk water, the line of C_V maxima is very close to the line obtained from the maxima of K_T but it is less affected by fluctuations. This is because we calculated C_V directly from the energy fluctuations while for K_T we had to use numerical derivatives since the number of molecules and the volume are kept fixed. The line of C_V maxima approxi-

mately identified with the WL is reported in the $\rho - T$ plane of Fig. 1.

According to previous work on bulk and confined water, we expect that at the crossing of the WL at constant density upon decreasing the temperature, the system would show a crossover from a fragile to a strong behavior in the dynamics of the density correlators. We note that a dynamical crossover also takes place in solvophobic solutions on crossing the WL.[81] To find the crossover in our aqueous solution, we performed calculations of the self-density correlator along paths at constant density by decreasing the temperatures from 300 K to 190 K. The range of densities investigated goes from $\rho = 0.95$ g/cm^3 to 1.10 g/cm^3.

IV. THE MCT TRANSITION

In order to study the dynamical behavior of water in the solution we calculated the SISF of the oxygens

$$F_{OO}^s(Q, t) = \frac{1}{N_w} \left\langle \sum_i e^{i\vec{Q}\cdot[\vec{R}_O(t) - \vec{R}_O(0)]} \right\rangle \qquad (2)$$

as function of the temperature for different values of the density. The F_{OO}^s has been calculated at $Q = Q_0$, the position of the maximum of the O–O structure factor ($Q_0 = 2.25$ Å^{-1}), for which the effects of supercooling are expected to be enhanced. We report in Fig. 2, as an example, the SISF for the density $\rho = 0.97$ g/cm^3. Upon supercooling, we observe that after the ballistic regime at very short time the correlators show a fast decay to a double dynamical behavior determined by the *cage effect*. At intermediate times it is observed the β-relaxation regime followed by the long time decay in the α-relaxation regime. Upon decreasing temperature, the particles are trapped for an increasing time in transient cages formed by their nearest neighbors. The relaxation of the cages enables the free diffusion of the particles with a consequent decay to zero of the correlator. This α-decay takes place with a stretched exponential form $e^{(-t/\tau)^\beta}$ where τ is the α relaxation time and β is called the Kohlrausch exponent. In order to combine the short and the long time behavior the curves in
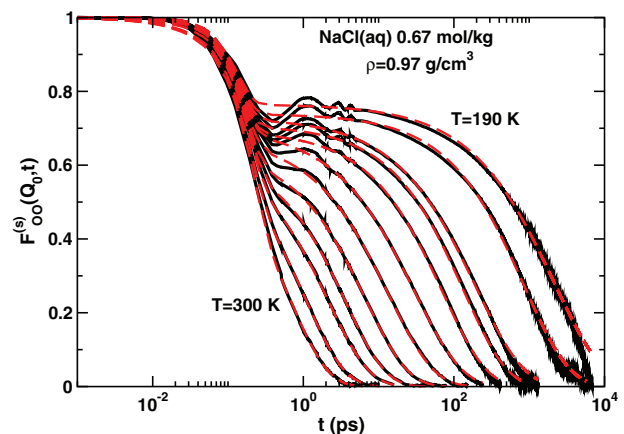

FIG. 2. SISF of the water oxygens in the mixture for the density $\rho = 0.97$ g/cm^3 for temperatures in K: 300, 280, 260, 250, 240, 230, 220, 215, 210, 205, 200, and 190. The broken lines are the fits obtained in Eq. (3).

TABLE II. Fitting parameters of the SISF with Eq. (3) for the density $\rho = 0.97$ g/cm^3.

T (K)	$A(Q_0)$	r_{cage} (Å)	τ_s (ps)	τ (ps)	β
300	0.634	0.520	0.221	0.679	0.869
280	0.655	0.501	0.204	1.054	0.822
260	0.638	0.516	0.193	2.117	0.786
250	0.627	0.526	0.182	3.631	0.815
240	0.642	0.512	0.174	6.737	0.772
230	0.676	0.482	0.162	13.67	0.726
220	0.701	0.459	0.153	29.97	0.689
215	0.693	0.466	0.153	71.00	0.746
210	0.708	0.452	0.147	134.3	0.753
205	0.728	0.434	0.142	197.8	0.685
200	0.739	0.423	0.139	861.5	0.723
190	0.765	0.398	0.133	2151.0	0.664

Fig. 2 can be fitted with the phenomenological formula[35, 36]

$$f^s(Q, t) = (1 - A(Q)) \exp[-(t/\tau_s)^2] + A(Q) \exp[-(t/\tau)^\beta],$$
(3)

where τ_s is the fast relaxation time. The normalizing coefficient $A(Q)$ corresponds to the Lamb-Mössbauer factor (LMF)[37, 82]

$$A(Q) = \exp\left(-r_{cage}^2 Q^2/3\right),$$
(4)

where r_{cage} is the radius of the cage. The fits are reported in Fig. 2 and the fitting parameters are reported in Table II. We note that the quality of the fits is very good.

From Table II, we note that below $T = 240$ K the shrinkage of the cage is stronger than in bulk TIP4P water[40] with a corresponding more rapid decrease of the fast relaxation time.

The most relevant quantity to determine the dynamics of supercooled water is the α-relaxation time τ. In the left panel of Fig. 3, it is shown that in a large range of temperature in the mild supercooled region a best fit of τ can be performed with the power law prediction of the MCT
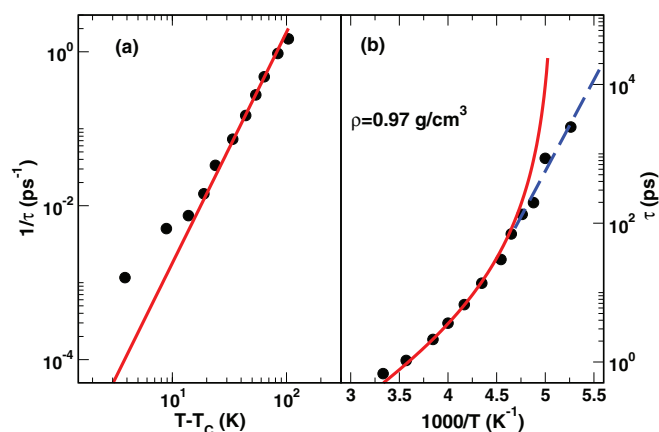
$$\tau = C (T - T_C)^{-\gamma},$$
(5)

FIG. 3. α-relaxation time of the oxygens for density $\rho = 0.97$ g/cm^3. Left panel: log-log plot of $1/\tau$ vs. $T - T_C$, the bold line is the fit to Eq. (5) with $T_C = 196.1$ K and $\gamma = 3.0$. Right panel: τ as function of the inverse temperature. The bold curve is the MCT fit while the dashed line is the fit to the Arrhenius behavior, see Eq. (6).
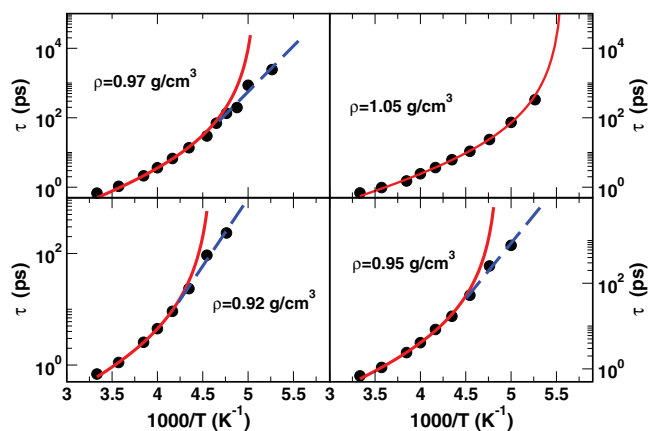

FIG. 4. α-relaxation time of oxygens as function of the inverse temperature for various densities as indicated in the respective panels. The bold curve is the MCT fit while the dashed line is the fit to the Arrhenius behavior (see Eq. (6)).

where T_C is the MCT crossover temperature. In the MCT framework T_C marks the crossover from a regime where the relaxation is determined by the breaking and reforming of the cages to a regime where the dynamics is arrested since the cages are frozen. MCT predicts this ergodic to non-ergodic ideal transition by neglecting the hopping effects that in most liquids intervene to restore ergodicity. Below T_C hopping effects are included in extensions of the MCT. The MCT fit for the $\rho = 0.97$ g/cm^3 isochore gives the value $T_C = 196.1$ K with an exponent $\gamma = 3.0$. It is evident that the fit can be realized only by excluding the lower temperatures. Below $T \approx 215$ K, τ can be fitted by an Arrhenius function

$$\tau = \tau_0 \exp(E_A/k_B T).$$
(6)

This indicates that for low enough temperatures solvent water has a strong behavior of the relaxation time, similar to the bulk. The right panel in Fig. 3 shows both the MCT fit and the Arrhenius fit with the activation energy $E_A = 50.4$ kJ/mol. Therefore, at around $T_L = 215$ K, the system shows a FSC in the behavior of the relaxation time.

The analysis performed for the density $\rho = 0.97$ g/cm^3 has been repeated for the other densities, $\rho = 0.92$ g/cm^3, $\rho = 0.95$ g/cm^3, $\rho = 0.98$ g/cm^3 and $\rho = 1.05$ g/cm^3. The α-relaxation time can be fitted with the MCT asymptotic law (5) in all the cases and for $\rho = 0.92$ g/cm^3 and $\rho = 0.95$ g/cm^3 it is found a FSC.

The results are reported in Fig. 4 ($\rho = 0.98$ g/cm^3 is not shown). We will discuss this FSC in Sec. V. This crossover was already found in pure TIP4P water[40] and, as stated above, in computer simulation of different models of water and confined water.[6, 24, 41, 57]

V. FRAGILE TO STRONG CROSSOVER AT THE WIDOM LINE

For each density the α-relaxation time can be fitted with the MCT asymptotic law (5). We note that for the highest density investigated, $\rho = 1.05$ g/cm^3 MCT is valid in all the range of temperature. In the other cases a temperature T_L marks the crossover of the dynamics of water in the supercooled

TABLE III. Parameters of the fit of the α-relaxation time τ with the MCT power law (5) and with the Arrhenius formula (6). The last column is the FSC temperature estimated from the numerical derivatives of τ vs $1/T$,[57] this procedure determines the crossing of the two curves with an estimated uncertainty of ± 1 K.

ρ (g/cm^3)	T_C (K)	γ	E_A (kJ/mol)	T_L (K)
0.92	216.3	2.19	46.3	240.0 ± 1.0
0.95	205.3	2.59	49.7	226.0 ± 1.0
0.97	196.1	3.00	50.4	215.0 ± 1.0
0.98	193.1	3.04	54.4	210.0 ± 1.0
1.05	179.1	2.77	...	...

solution from the fragile to the strong behavior. The results are summarized in Table III.

It is evident that the ideal MCT transition is shifted to lower temperatures at increasing density. The deviation from the MCT fragile behavior is determined by hopping effects that intervene to turn on an activated dynamics described by the Arrhenius exponential law. The behavior of the FSC temperature indicates that increasing density displaces hopping effects to lower temperature except for the highest density where the FSC does not take place.

We report in Fig. 5 the T_L in the $\rho - T$ plane together with the LMS, the WL, and the TMD curve. We observe that the FSC points follow the WL with a trend similar to the results obtained in pure TIP4P water. The density $\rho = 1.05$ g/cm^3 lies above the WL in the region where water is in the HDL phase. It shows a fragile behavior and the FSC is not observed at least for the lowest temperature that it was possible to investigate.

Our observations are perfectly consistent with the hypothesis that crossing the WL upon supercooling favors hopping. In Fig. 6, we report the MCT T_C as obtained from the fit of the power law and the FSC temperature T_L in the $\rho - T$ plane for the ionic solution and for the bulk.[40] The effect of the ions is a shift of the WL to lower density and higher temperature with respect to pure water and as a consequence it is observed the same kind of shift for the curve collecting the FSC points. The ions enlarge the region of stability of the HDL, as established in previous simulations[70] and interestingly found also in LiCl(aq).[63] From Fig. 6, it is also evident
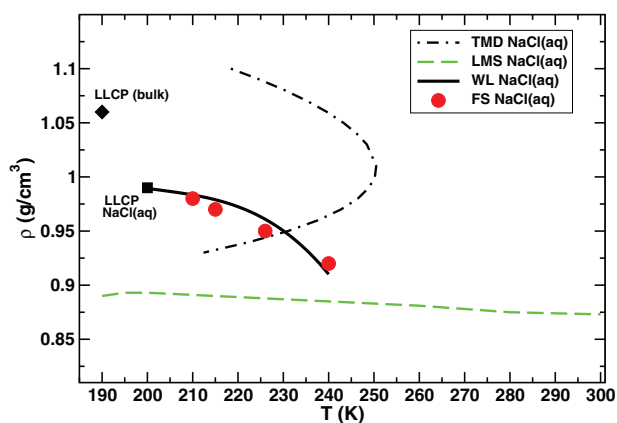

FIG. 5. Phase diagram already shown in Fig. 1 with the addition of the points of the estimated location of the fragile to strong crossover.
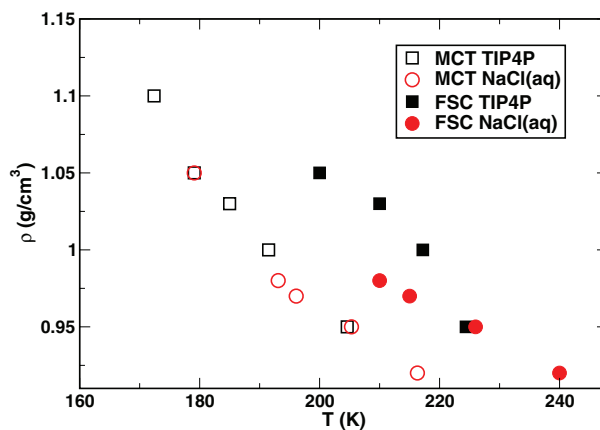

FIG. 6. In the $\rho - T$ plane: MCT crossover points for pure TIP4P water (open squares) and for NaCl(aq) (open circles), FSC points for pure TIP4P water (full squares), and for NaCl(aq) (full circles).

that the MCT crossover T_C is almost unaffected from the addition of ions at least at this concentration. This means that ions intervene in modifying hopping more than mechanisms which cause cage relaxation.

VI. CONCLUSIONS

Dynamical properties of water as solvent in a NaCl(aq) solution at concentration of 0.67 mol/kg have been studied upon supercooling by MD simulations. The system is simulated by combining the TIP4P model and the Jensen-Jorgensen ion-ion and ion-water potential. The behavior of the self-intermediate scattering function of the water oxygens has been calculated along isochores that starts from $T = 300$ K and crosses the WL by decreasing the temperature.

Below $T = 300$–280 K the double relaxation regime takes place after the ballistic transient. The long time decay can be described by a stretched exponential function determined by the α-relaxation time $\tau(T)$. The behavior of τ for all the densities and in a large range of temperature upon supercooling can be fitted with the prediction of the MCT. The MCT temperatures T_C of the ideal crossover from the ergodic behavior to non-ergodicity have been determined. The values of T_C are found very similar to the ones obtained in pure water. This implies that ions, at least at this concentration, have little effect on the ideal MCT transition.

For the densities below the estimated critical density of the LLCP when the simulation path along the isochore crosses the WL the relaxation time τ shows a crossover from the MCT fragile to a strong Arrhenius behavior. This crossover is not present for the density above the critical density where water is in its HDL phase down to the lowest temperature where supercooling was possible. For this density the behavior of the liquid remains fragile.

Our results show that the WL determines the FSC in the ionic solutions in the same way and on the same grounds as in pure water, showing that also in solutions hopping is more favored where water is less dense.

The connection found between the dynamic and the thermodynamic behavior upon approaching the LLCP and along

the WL in bulk water and here in the NaCl aqueous solution can provide a further tool for the investigation of the liquid-liquid transition in experiments. In the solution, the LLCP moves at higher temperature and lower temperatures and this can be exploited in investigations of aqueous solutions by experiments able to probe the dynamics.

We also note here that the ideal probes for this kind of phenomenology are those who probe directly translational dynamics with no coupling to rotations and in the time scale from ps to ns and spatial range from fraction to tenths of Å, for example, quasi elastic neutron scattering (QENS). Thermal neutrons in fact directly couple to density fluctuations and the energy and Q ranges of QENS are within the proper window so that they can be safely compared to results on translational diffusion in simulation.

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