

Slow glassy dynamics and fragile-to-strong crossover in supercooled aqueous magnesium perchlorate solutions: The effect of Martian solutes

P. La Francesca , L. Lupi , and P. Gallo *

Dipartimento di Matematica e Fisica, *Università degli studi Roma Tre*, Via della Vasca Navale 84, 00146 Roma, Italy



(Received 12 February 2026; accepted 17 August 2026; published 15 September 2026)

The dynamical behavior of water in magnesium perchlorate aqueous solutions is investigated through molecular dynamics simulations using the TIP4P/2005 water model and the recently extended Madrid-2019 force field. This study is motivated by the recent radar detection of liquid water underneath the Martian South Pole. We explore the supercooled regime for salt concentrations up to 24.4 wt %. In the region of mild supercooling we analyze the water oxygen self-intermediate scattering functions. Our results show that the relaxation dynamics of water is well described by the mode coupling structural relaxation in this region. Upon further cooling, a fragile-to-strong crossover is observed for all investigated concentrations. Below the crossover, activated processes maintain the ergodicity. Notably, the addition of magnesium perchlorate induces a downward shift in both the mode coupling temperature and the fragile-to-strong crossover temperature. This combined effect extends the range of existence of the supercooled liquid regime to lower temperatures compared to bulk water. These findings support the hypothesis that perchlorate aqueous solutions can persist in a thermodynamically metastable liquid state at the low-temperature conditions of the Martian subsurface.

DOI: [10.1103/hpn9-7sls](https://doi.org/10.1103/hpn9-7sls)

I. INTRODUCTION

Within the framework of statistical mechanics and condensed matter physics, the study of water and aqueous solutions stands out as one of the most intensely researched fields [1–6]. In particular, aqueous solutions of perchlorates are also of specific interest to the planetary science community following radar anomalies connected to the possible existence of liquid water under the Martian South Pole crust and detected by the MARSIS instrument [7,8]. In this context, it is important to understand how bulk water properties transfer to solutions, especially at low temperatures, and to establish whether the limit of supercooling can be extended.

Liquid water exhibits a large number of anomalies; the most well known of these is the presence of a temperature of maximum density (TMD) in its phase diagram. Moreover, when water is supercooled, i.e., when kept liquid below its freezing temperature, it features a remarkably sharp increase of its thermodynamic response functions, which appear to diverge following power laws typical of critical phenomena.

While the supercooling of bulk water is easily attained by molecular dynamics simulations because of the fast cooling rates, experimentally it is possible to supercool water only until nucleation intervenes. Nonetheless, there is no thermodynamic barrier preventing supercooled water from reaching

a glassy state through a reversible path [9] and, in fact, recent experiments have entered the previously inaccessible region of deep supercooling known as “no-man’s land” [10–13]. However, the unavoidable presence of impurities facilitates the nucleation, as the intrinsic tendency of water to arrange into distorted tetrahedral structures serves as precursor for ice crystallization [2].

The dynamical behavior of bulk water in the mildly supercooled regime is successfully described within the framework of the mode coupling theory (MCT) [14]. Although originally formulated for simple liquids undergoing a glass transition, the MCT predictions have been shown to capture the features of the glassy dynamics of supercooled water with remarkable accuracy [15,16]. The validity of the theory has been extensively verified not only for the bulk phase [15–20], but also under confinement [21–24] and in ionic aqueous solutions [25,26]. Moreover, recent studies have shown that the MCT can be extended to describe the dynamics of water solvating biomolecules and of bioaqueous solutions [27–34].

An important aspect of water glassy dynamics at low temperatures is the existence of a dynamic fragile-to-strong crossover (FSC). While at moderate supercooling water behaves as a fragile liquid, typically following the power-law divergence predicted by the MCT, further cooling reveals a shift to a strong, Arrhenius-like behavior. This crossover has been found and extensively studied in simulations [18,35,36], it has been found in experiments and simulations in confinement [37–39], and, recently, experimentally also in bulk water [40].

In the supercooled region, a second-order liquid-liquid critical point (LLCP) is supposed to exist. First proposed by Poole *et al.* in 1992 [41] on the basis of molecular dynamics (MD) simulations, this hypothesis theorizes that below the

*Contact author: paola.gallo@uniroma3.it

liquid-liquid critical temperature water exists in two liquid phases: high-density liquid (HDL) and low-density liquid (LDL). Simulations have since found the LLC in several water models [42–53]. Substantial experimental evidence supports the LLC scenario [11,12,54–57] and recently the vicinity of the LLC has been probed [58]. Interpreting water’s thermodynamic anomalies as consequences of the LLC provides a coherent and unified description of the phenomenology of supercooled water.

The study of aqueous solutions is strongly intertwined with that of the bulk. Aqueous solutions can provide, in fact, easier access to the supercooled regime compared to bulk water [59–61]. Besides, the peculiar features of supercooled water have been shown to persist in several aqueous solutions for concentrations from low to mild [25,33,34,56,60,62–67]. For instance, experiments have shown that water anomalies persist in aqueous solutions of sodium perchlorate up to 2 M [68].

In order to explore the limits of supercooling on Mars we focus here on the dynamical behavior of relevant aqueous solutions. In this work, we investigate the slow dynamics of supercooled water for magnesium perchlorate aqueous solutions $[\text{Mg}(\text{ClO}_4)_2]$ upon supercooling to test the MCT behavior, to find its range of validity, and to study the occurrence of a crossover to a strong behavior. As experimental analyses point to the existence of liquid perchlorate solutions located approximately 1.5 km underneath the Martian South Pole [7,8], understanding the dynamical behavior of water in these conditions holds significant relevance.

This study follows previous investigations of the thermodynamics and structure of magnesium, calcium, and sodium perchlorate solutions [69–71]. In these works, the persistence of several water anomalies was observed, including an interplay between HDL-like and LDL-like structural environments. It was also found that, overall, the HDL-like behavior becomes more accentuated as the salt concentration increases. Furthermore, the liquid-liquid critical point (LLCP) appears to survive at least at low concentrations.

The paper is organized as follows. In Sec. II, we describe the molecular dynamics simulations and the system details, including the specific concentrations of magnesium perchlorate investigated. In Sec. III, we present the analysis of the self-intermediate scattering functions and the evaluation of the fragile-to-strong crossover. Finally, in Sec. IV the conclusions are presented.

II. METHODS

We performed classical molecular dynamics (MD) simulations [6,72] of magnesium perchlorate aqueous solutions at different concentrations using the GROMACS 5.1.4 software package [73,74].

Water was modeled using the TIP4P/2005 potential [75], and the magnesium ion using the Madrid-2019 force field [76], while the perchlorate ion was modeled using its recent extension introduced in Ref. [77] (flexible model A). The Madrid-2019 force field has been explicitly designed to work with TIP4P/2005. It shows good performances for solubility, for density, and transport properties, compared to experiments.

TABLE I. Concentrations of the four systems investigated.

$N_{\text{Mg}(\text{ClO}_4)_2}$	$N_{\text{H}_2\text{O}}$	Conc. (wt %)
0	4000	0
10	4072	2.95
35	3900	10.0
100	3838	24.4

The Hamiltonian equations were integrated using the leap-frog algorithm with a time step of 1 fs. Three-dimensional periodic boundary conditions were applied. All bond lengths were constrained using the LINCS algorithm [78]. Short-range nonbonded interactions (both van der Waals and electrostatic) were truncated at a cutoff distance of 0.95 nm. Long-range dispersion corrections were applied for both energy and pressure. Long-range electrostatic interactions were treated using the particle mesh Ewald method [79].

Simulations were performed in the isothermal-isobaric (N - P - T) ensemble. The temperature was controlled using the Bussi-Donadio-Parrinello thermostat [80], while the pressure was maintained at 5 MPa using the isotropic Parrinello-Rahman barostat [81,82].

We investigated solutions at the concentrations reported in Table I. At each concentration, we studied the system gradually lowering the temperatures from 300 to 200 K. At $C = 10.0$ wt % we supercooled down to 190 K and at $C = 24.4$ wt % down to 180 K. Both the equilibration and the production runs were performed increasing, upon cooling, the run time from 1 to 100 ns.

The pressure and temperatures investigated were chosen for their relevance to subglacial Martian conditions [83]. From the MD trajectories we computed the observables described in the next section.

In Fig. 1 we show a snapshot of the 24.4 wt % aqueous solution investigated for $T = 200$ K.

III. RESULTS

A. Mode coupling theory analysis

The MCT provides a microscopic framework to describe the dynamics of supercooled liquids as they approach the glass transition. As the liquid is supercooled, the dynamical behavior of a particle evolves through distinct temporal stages. Initially, the particle exhibits free, ballistic motion. Subsequently, the so-called cage effect emerges: the particle becomes trapped by the local configuration of its nearest neighbors, restricting its movement to a confined spatial region. Only after a long transient does the particle escape this cage, transitioning into a long-time diffusive regime.

To analyze the translational dynamics, we studied the self-intermediate scattering function $F_s(\vec{q}, t)$ for the water oxygens. This is the Fourier transform of the Van Hove self-correlation function and it is defined as

$$F_s(\vec{q}, t) = \frac{1}{N_{\text{Ow}}} \left\langle \sum_{k=1}^{N_{\text{Ow}}} e^{i\vec{q} \cdot [\vec{r}_k(t) - \vec{r}_k(0)]} \right\rangle. \quad (1)$$

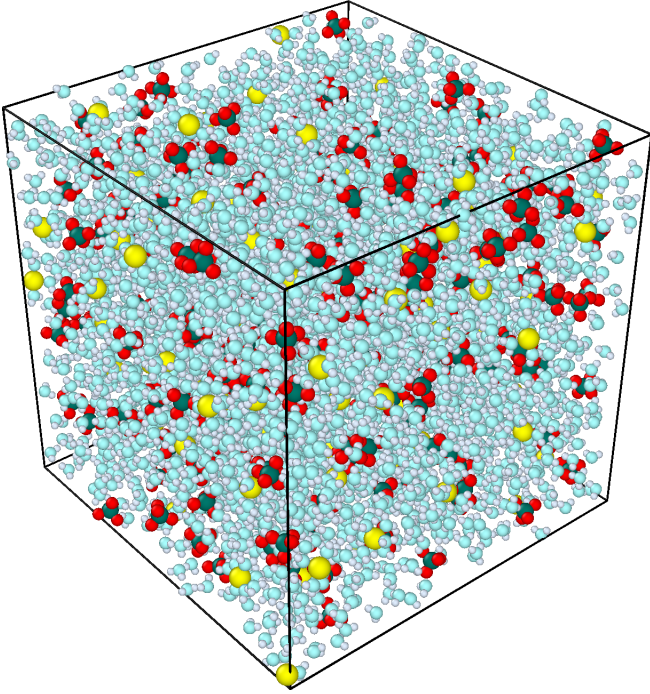


FIG. 1. Snapshot of a 24.4 wt % aqueous magnesium perchlorate solution at $p = 5$ MPa and $T = 200$ K. The water molecule is shown in light gray and light turquoise, the magnesium ion in yellow, and the perchlorate ion in dark teal (chlorine) and red (oxygens).

Here, $\vec{r}_k(t)$ denotes the position of the oxygen atom of the k th water molecule at time t , $\vec{q}$ is the transferred wave vector, and the sum runs over all the N_{O_w} water oxygens.

The self-intermediate scattering functions have been computed for all investigated concentrations and temperatures at $q_0 = 22.5 \text{ nm}^{-1}$ and are reported in Fig. 2. The wave vector q_0 corresponds to the position of the first peak of the oxygen-oxygen static structure factor of the TIP4P/2005 model [75], where the MCT features of water are best evident. It can be observed that at high temperatures, the curves decay rapidly to zero. Upon cooling, a two-step relaxation mechanism emerges, which is the signature of glassy dynamics described by the MCT. Following the initial ballistic regime, indeed, an intermediate dynamical region known as the β -relaxation region emerges. As the temperature decreases, this feature evolves from a simple inflection point into a distinct plateau, reflecting the transient trapping of water molecules within the cage formed by their nearest neighbors. The length of this plateau extends significantly upon supercooling, signaling a more persistent caging effect and a further slowdown of the dynamics. Eventually, the cage breaks as the system enters the α -relaxation regime.

The self-intermediate scattering function can be modeled using the following expression [15,16]:

$$F_s(q, t) = [1 - f_q] e^{-(t/\tau_s)^2} + f_q e^{-(t/\tau_\alpha)^{\beta_\alpha}}, \quad (2)$$

where the initial Gaussian term accounts for the short-time ballistic motion with a characteristic time τ_s and the second term captures the slow decay of the $F_s(q, t)$ to zero following the cage breaking. This second process, known as the α relaxation, is characterized by a temperature-dependent

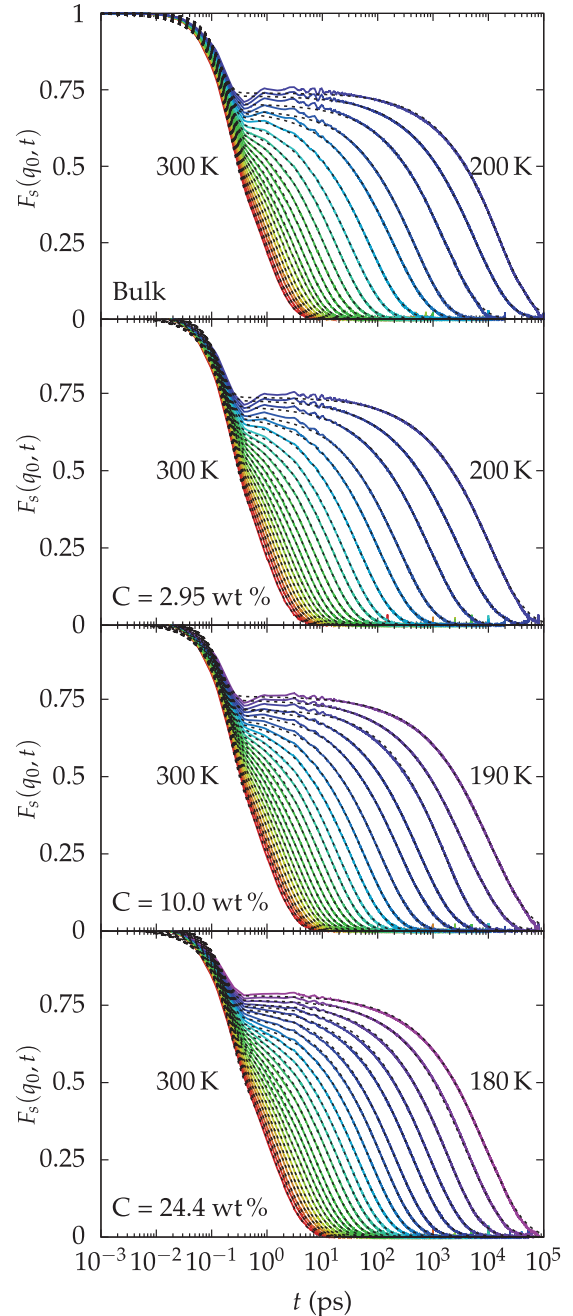


FIG. 2. Oxygen self-intermediate scattering functions with $q_0 = 22.5 \text{ nm}^{-1}$ for bulk water and magnesium perchlorate solutions at concentrations 2.95, 10.0, and 24.4 wt %. The curves cover the temperature range from 300 K to minima that range from 200 to 180 K. Dashed lines represent the fits to the MCT equation (2).

relaxation time τ_α and a stretching exponent β_α , while the Lamb-Mössbauer factor f_q represents the plateau height.

The results of the fitting procedure of $F_s(q_0, t)$ using the MCT functional form provided in Eq. (2) for the considered systems are also reported in Fig. 2 as dashed black lines, showing that the theoretical model reproduces the simulation over the entire range of validity.

From the fitting procedure, we extracted the fast relaxation time τ_s , the structural relaxation time τ_α , the f_q parameter,

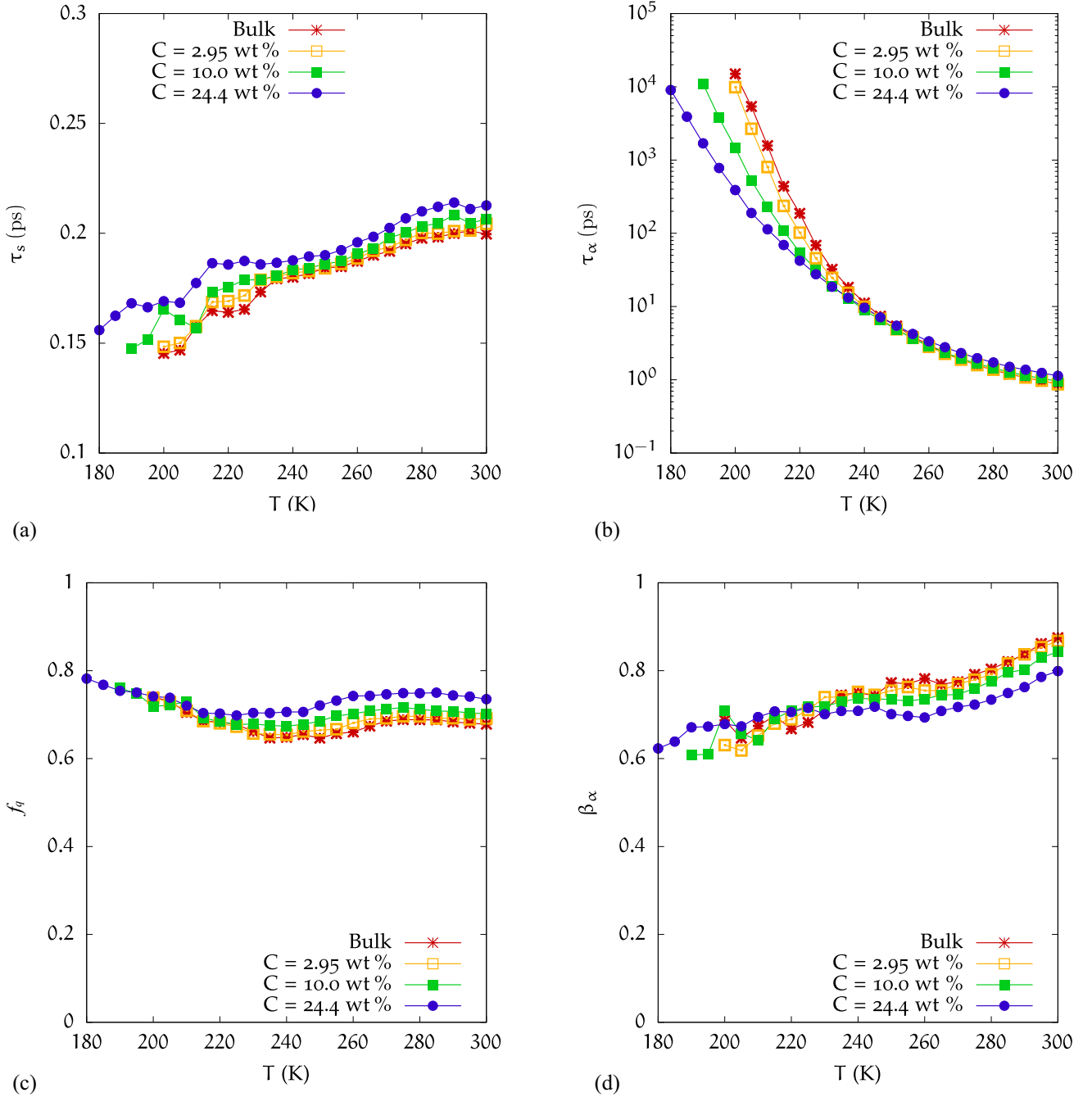


FIG. 3. Temperature dependence of the MCT fitting parameters for bulk water and magnesium perchlorate solutions at different concentrations: (a) the fast relaxation time τ_s , (b) the structural relaxation time τ_α , (c) the Lamb-Mössbauer factor f_q , and (d) the stretching exponent β_α .

and the stretching exponent β_α for the bulk and at all the concentrations investigated.

The fast relaxation time τ_s [Fig. 3(a)] describes the short-time dynamics associated with the motion of water molecules within the cage. This parameter exhibits a weak temperature dependence, varying within the range of 0.14–0.22 ps, and decreasing slightly upon cooling. We can see that the behavior of τ_s in the solutions is similar to the bulk and the dependence on salt concentration is marginal.

The structural relaxation time τ_α is shown in Fig. 3(b) at different values of T . A strong temperature dependence is evident at all concentrations, as lower temperatures suppress the system's ability to reorganize. At high temperatures, the relaxation times increase with increasing salt concentration, with bulk water exhibiting the fastest dynamics and the 24.4 wt % solution the slowest. However, as the temperature decreases, the gap between the curves corresponding to the bulk, the 2.95 wt %, and the 10.0 wt % solutions progressively narrows, until visible crossovers occur in the range

265 K $\lesssim T \lesssim$ 270 K. A similar trend, involving the 24.4 wt % solution, is observed between 235 and 250 K. Hence, at low temperatures, the hierarchy of the relaxation times is inverted: bulk water exhibits the steepest increase in τ_α , becoming the slowest system, whereas the most concentrated solution exhibits faster water dynamics. We analyze in Sec. III B the glassy behavior of τ_α and we discuss in Sec. III D how these crossings at different concentrations are related to the diffusion anomaly of water.

The Lamb-Mössbauer factor, f_q , reported in Fig. 3(c), represents the height of the plateau and it is related to the length of the localization induced by the cage. We observe that f_q generally increases with concentration and exhibits a mild dependence on temperature. The Lamb-Mössbauer factor satisfies [15]

$$f_q = e^{-\frac{a^2}{3} q^2},$$

with a being the radius of the cage. We found the average values of a to be 0.048 nm for the bulk, 0.047 nm for the 2.95 wt % solution, 0.046 nm for the 10.0 wt % solution, and 0.043 nm for the 24.4 wt % solution. Overall, the trend of the f_q appears to be similar to the bulk with a slight temperature dependence.

Finally, Fig. 3(d) displays the temperature dependence of the stretching exponent β_α characterizing the structural relaxation. For all concentrations, the values of β_α fall within the range typically predicted by the mode coupling theory. As for the bulk, for each concentration a decrease in β_α is observed upon cooling, indicating that the relaxation dynamics becomes progressively more stretched at lower temperatures.

B. Fragile-to-strong crossover

The fragile-to-strong crossover is connected to the underlying thermodynamics of the system: according to the theory of critical phenomena, the approach to a second-order critical point is preceded by precursor phenomena, namely, the maxima in thermodynamic response function, accompanied by a line of maxima of the correlation length, known as the Widom line [84]. In the LLCP scenario, this line marks, within the one-phase region, the boundary between thermodynamic states dominated by HDL-like or LDL-like fluctuations. Therefore, the apparent divergences of the thermodynamic response functions, like κ_T and c_V , measured experimentally for water in the one-phase region, are the initial increase of the maxima of the Widom line.

Both simulations and experiments have confirmed the existence of this line in the supercooled region of water, further supporting the LLCP hypothesis [11,18,35,84–86]. Importantly, the FSC has been found to occur in coincidence with the crossing of the Widom line [20,22,25,36,85]. In this scenario, the crossover marks the structural evolution from an HDL-dominated regime to an LDL-dominated regime, where the dynamics becomes governed by activated hopping processes that have been shown to be favored when water is less dense [19].

In order to identify the FSC, the structural relaxation times τ_α are plotted in Fig. 4 as a function of the inverse temperature.

Within the MCT framework, upon moving along a path of constant pressure (or density) and decreasing temperature,

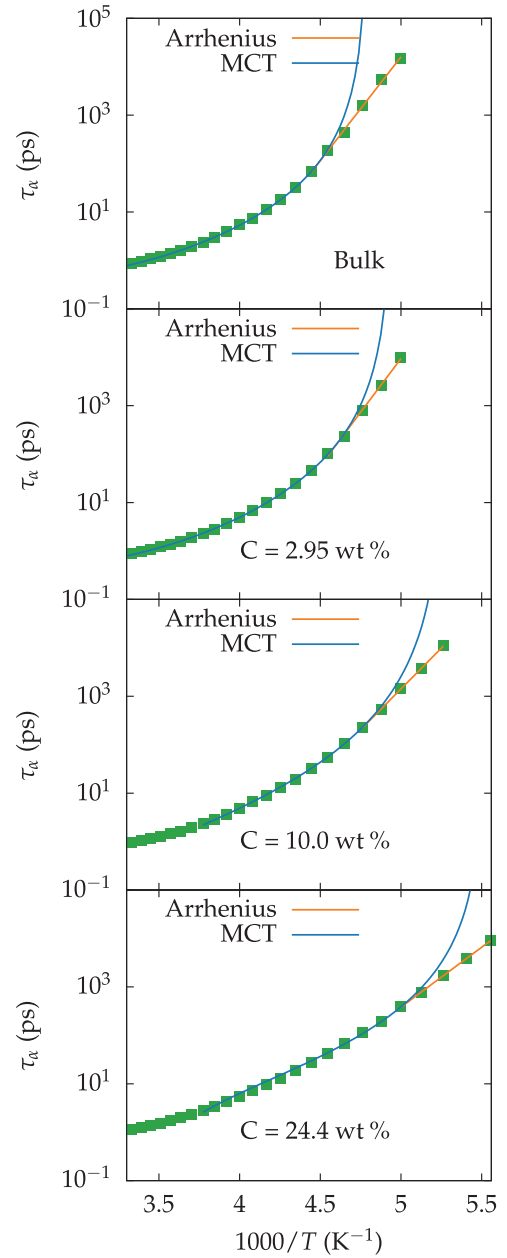


FIG. 4. Plots of the α -relaxation times τ_α for bulk water and solutions at different concentrations. The blue solid lines represent the MCT power-law fits (fragile regime), while the orange solid lines represent the Arrhenius fits (strong regime).

below a certain mode coupling temperature T_c the $F_s(q, t)$ correlator does not decay to zero. Ideally, in this phase, structural arrest occurs, the ergodicity is broken, and the system vitrifies. Ideally, hence, the relaxation time τ_α diverges upon approaching T_c following a power law predicted by the MCT:

$$\tau_\alpha \sim (T - T_c)^{-\gamma}. \quad (3)$$

The physics of the FSC can be interpreted through the underlying free-energy landscape. At temperatures lower than T_c , the free-energy landscape features a large number of local minima separated by energy barriers that break the ergodicity of the system. In real glass formers, unlike the idealized MCT

TABLE II. Fitting parameters for the structural relaxations and fragile-to-strong crossover temperatures at different concentrations. T_c and γ come from the MCT fit, E_A from the low-temperature Arrhenius fit.

System	γ	T_c (K)	E_A (kJ/mol)	T_{FSC} (K)
Bulk	2.78	208.9	82.0	225
2.95 wt %	3.06	202.4	84.8	220
10.0 wt %	3.51	189.8	64.4	210
24.4 wt %	2.94	181.3	47.3	200

prediction, the $F_s(q, t)$ decays to zero even below T_c . This is because ergodicity is restored by thermally activated hopping processes, which allow the system to escape the local minima.

Consequently, close to the ideal glass transition, the system undergoes a crossover. The region where the liquid follows the MCT power law is associated with *fragile*, MCT behavior. Upon further supercooling, when hopping processes dominate the dynamics, the relaxation time deviates from the MCT prediction and follows an Arrhenius law:

$$\tau_\alpha = \tau_0 \exp\left(\frac{E_A}{k_B T}\right), \quad (4)$$

where E_A is the activation energy and k_B the Boltzmann constant. This regime is defined as *strong*. The temperature at which this change in dynamical behavior occurs is identified as the FSC temperature. For bulk water, early computer simulations of water using the SPC/E potential found such a crossover, which was later confirmed by experiments and simulations in confined water [37–39]. Importantly, the FSC in bulk water has been recently measured [40]. The FSC has been found to occur upon crossing the Widom line for several water models, pointing to the region where the LLCP is predicted to be located [18,85,86].

Consistent with the MCT predictions, as per Fig. 4, in the mild supercooled region the values of τ_α fitted in the previous section follow the power-law divergence described by Eq. (3). The power-law fit is indicated by the blue lines in Fig. 4. As the temperature is further lowered, the relaxation times deviate from the MCT prediction. This deviation marks the onset of activated hopping processes, which restore ergodicity. In this deep supercooled regime, the temperature dependence of τ_α exhibits an Arrhenius behavior, defined by Eq. (4), as shown by the orange lines in Fig. 4. The crossover temperature T_{FSC} was determined as the intersection point between the MCT power-law fit and the Arrhenius fit. Our analysis reveals that the FSC is preserved in the presence of magnesium perchlorate at least up to the highest concentration investigated (24.4 wt %), suggesting that this mechanism survives in the ionic solutions investigated. However, the specific value of T_{FSC} and the activation energy E_A in the strong regime are influenced by the salt concentration.

The resulting fitting parameters are listed in Table II. We note that there is a downward shift in T_{FSC} upon increasing the concentration of the solutes. Furthermore, the bulk T_{FSC} is also in good agreement with literature results at the corresponding density [18]. We also note that T_c decreases substantially for the two lowest concentrations with respect to the bulk. This

TABLE III. Parameters from the MCT test.

Conc.	$f_q^{(vS)}$	$h_q^{(vS)}$	b	a	λ	γ
Bulk	0.719	0.497	0.456	0.272	0.812	2.93
2.95 wt %	0.742	0.510	0.430	0.263	0.812	3.06
10.0 wt %	0.774	0.522	0.399	0.251	0.810	3.24
24.4 wt %	0.771	0.524	0.469	0.277	0.809	2.88

means that the region of existence of the supercooled liquid phase extends downward in temperature, strengthening the hypothesis that the liquid-liquid critical point (LLCP) shifts toward lower temperatures upon addition of perchlorates, as conjectured in Ref. [70].

These results have important implications for the stability of liquid water on Mars. The downward shift of both the MCT temperature T_c and the crossover temperature T_{FSC} implies an increased stability of the supercooled region of water upon addition of ions down to significantly lower temperatures compared to the bulk. In particular, the lowering of both T_c and T_{FSC} extends the range of ergodicity of supercooled liquid water, thus delaying the onset of structural arrest. At the same time, the extension of the fragile regime renders the LDL phase increasingly unfavorable, hence reducing the occurrence of nucleation. The interplay of these effects provides support to the hypothesis that brines can persist in a supercooled liquid state at very low temperatures.

C. von Schweidler law

The MCT predicts that the stage of the β relaxation where the $F_s(q, t)$ departs from the plateau and enters the α -relaxation regime is described by a master curve,

$$\phi_q(t/\tau_\alpha) = f_q^{(vS)} - (t/\tau_\alpha)^b h_q^{(vS)}, \quad (5)$$

on which the self-intermediate scattering functions collapse at every temperature as a function of t/τ_α . Equation (5) is the von Schweidler law, $f_q^{(vS)}$ is the ergodicity factor, $h_q^{(vS)}$ is the amplitude, and b is the von Schweidler exponent.

Figure 5 shows the master plot obtained by plotting the $\{F_s(q_0, t)\}$ at different temperatures as functions of t/τ_α and their corresponding fits according to the von Schweidler law, the parameters of which are reported in Table III. The superposition of these curves with the master curve holds within the range of validity of Eq. (5).

We note that the MCT exponents and parameters extracted with the von Schweidler law do not change significantly with respect to the bulk and upon increasing the solute concentrations.

The exponent b is related to another parameter that characterizes the early stage of the β relaxation, the exponent a , through the exponent parameter λ , defined by the relation

$$\lambda = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)} = \frac{\Gamma^2(1-a)}{\Gamma(1-2a)}. \quad (6)$$

Here Γ is the Euler gamma function. The values of a obtained by inverting this equation are also reported in Table III.

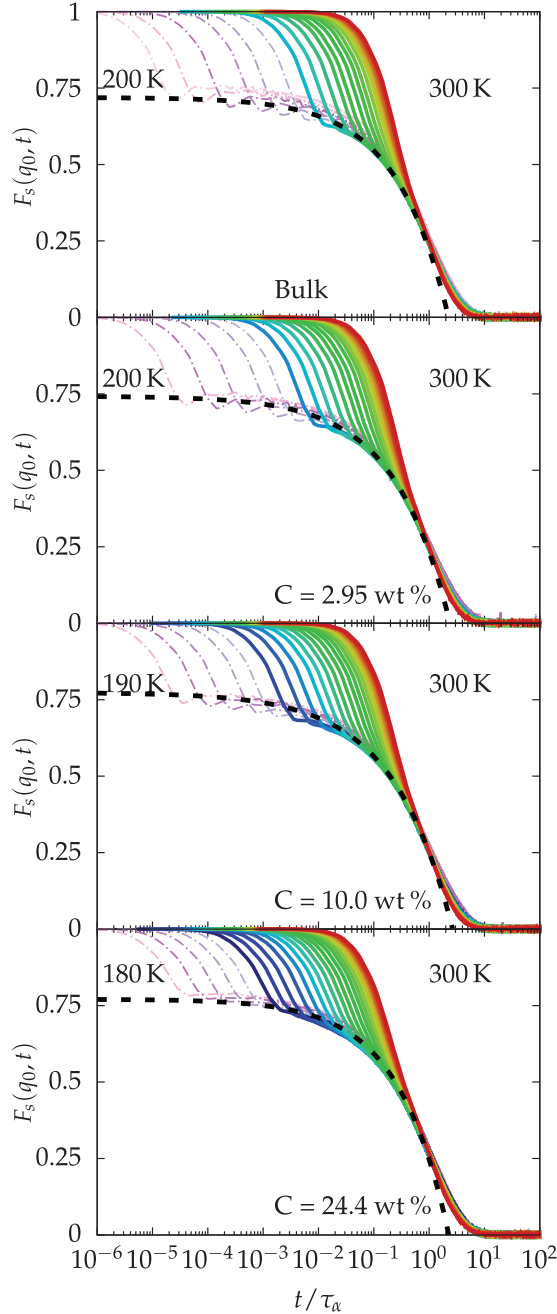


FIG. 5. Self-intermediate scattering functions vs scaled time t/τ_α for the four different systems considered. The thinner dash-dotted curves are those at $T \leq T_{\text{FSC}}$. The thick dashed curve is the master curve fitted from the von Schweidler law.

Furthermore, the parameters a and b are linked to the power-law exponent of the MCT scaling law via

$$\gamma = \frac{1}{2a} + \frac{1}{2b}. \quad (7)$$

These values are also reported in Table III and are in good agreement with those obtained from the MCT fit (Table II). The slight discrepancy may be attributed to hopping phenomena, which are known to already appear at the lower boundaries of the range of validity of the MCT [19].

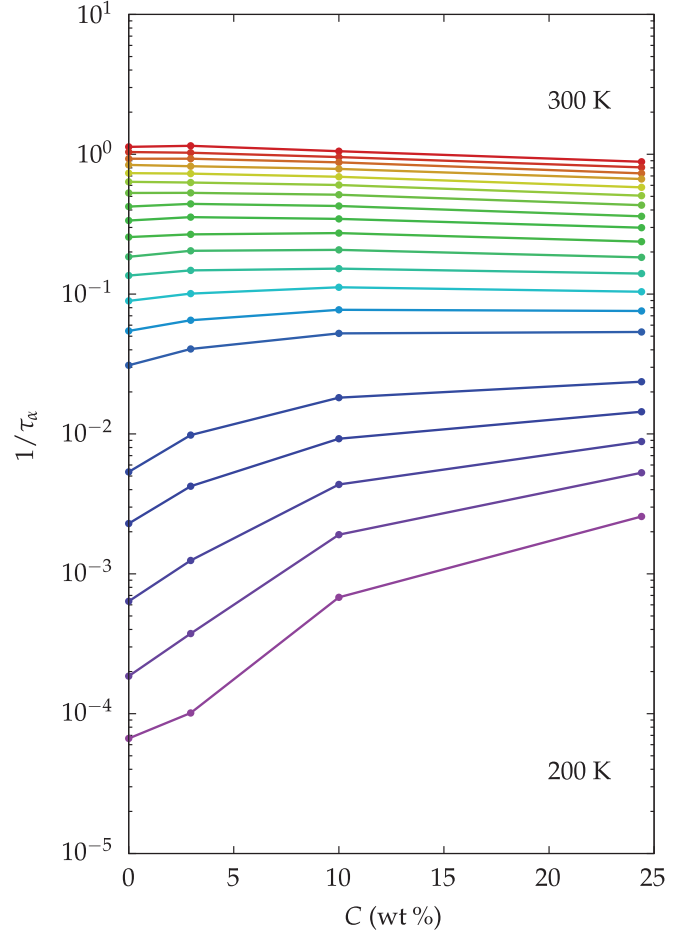


FIG. 6. Inverse of the relaxation times as a function of the solute concentrations for the different temperatures investigated down to 200 K.

D. Density analysis

The previously reported graph of τ_α in Fig. 3(b) shows that its high-temperature values increase upon increasing concentrations, whilst at low temperatures this trend is inverted. To better visualize this effect, in Fig. 6 we also plot τ_α^{-1} versus C at each of the considered values of T .

From this figure, we better appreciate that while at high temperatures, water in the solutions gets slower for higher concentrations, at low temperature the behavior is inverted.

The fact that, upon increasing concentration of solutes, water accelerates with respect to the bulk and to the lower concentrations, for low temperatures, is counterintuitive.

To provide a microscopic explanation for this dynamical behavior observed, we analyze how the water density is structurally affected by the presence of magnesium perchlorate. This low-temperature acceleration of water has been previously observed in aqueous solutions [31] and attributed to the diffusion anomaly of water [37,87].

Figure 7 shows the total density of the simulated systems along the 5 MPa isobar as a function of temperature. As expected, the global density increases significantly with salt concentration. Bulk water exhibits the characteristic temperature of maximum density (TMD) around 275 K for the

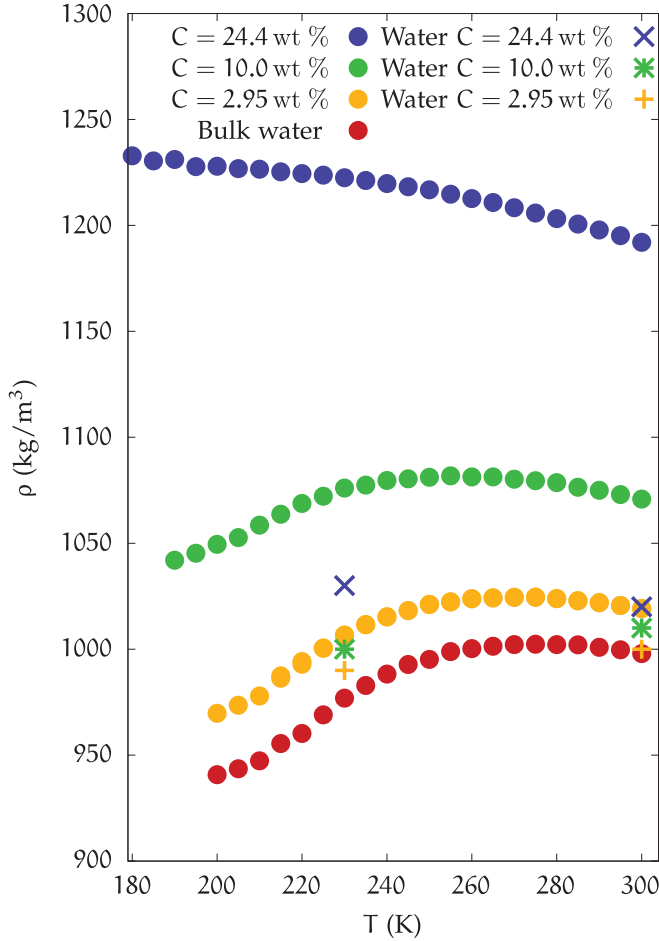


FIG. 7. Densities as a function of temperature for bulk water and magnesium perchlorate solutions at different concentrations (2.95, 10.0, and 24.4 wt %) along the 5 MPa isobar. Also plotted in the figure is the effective density of water in the solutions at $T = 230$ K and $T = 300$ K.

TIP4P/2005 model. Furthermore, the 2.95 and the 10.0 wt % solutions also exhibit a TMD, which shifts progressively toward lower temperatures as the salt concentration increases. For the 24.4 wt % solution, we do not observe the occurrence of the TMD at least down to the lowest temperature investigated. Below the TMDs observed, the density decreases, reflecting the onset of the water density anomaly, still maintaining the total values of the density significantly higher than in bulk water at all temperatures.

Since the total density reported in Fig. 7 includes the mass of the heavy ions, to find the real local density that water experiences we employed a mapping procedure based on the oxygen-oxygen radial distribution functions (RDFs) $g(r)$. We estimated the effective density of water in the solution by comparing the $g(r)$ of water in the solutions with the $g(r)$ of pure bulk TIP4P/2005 water simulated at different densities and finding those that match the best. The match was determined quantitatively by evaluating the sum of squared residuals between the $g(r)$ of the solution and the reference bulk simulations over a spatial range near the first minimum. This procedure was also used in Refs. [31,34].

Figure 8 shows the results for the three concentrations. For the lowest concentration [2.95 wt %, panel (a)], the RDF of water in solution at 230 K is best reproduced by bulk water at a density of 990 kg/m^3 . Considering that the density measured from the simulations for pure TIP4P/2005 water at this temperature is 977 kg/m^3 , this indicates that the water structure in the dilute solution is already more compressed than in the bulk. This local densification increases with concentration. For the 10.0 wt % solution [panel (b)], the effective water density at 230 K rises to 1000 kg/m^3 , and at 24.4 wt % [panel (c)], it reaches 1030 kg/m^3 . Similarly, at $T = 300$ K, the effective density of water is 1000 kg/m^3 at 2.95 wt %, 1010 kg/m^3 at 10.0 wt %, and 1020 kg/m^3 at 24.4 wt %. The estimated values of density of water for these two temperatures are also reported in Fig. 7.

These results provide the structural key to interpreting the dynamical crossover where solutions become faster than bulk water. In the bulk phase, cooling leads to a more pronounced density decrease associated with the formation of a tetrahedral LDL network, as the occurrence of the fragile-to-strong crossover upon decreasing the temperature is associated with the crossing of the Widom line [18].

In contrast, the fact that water in the solutions appears faster than the bulk is a direct consequence of the comparison not being made at the same effective water density. In perchlorate solutions, in fact, the ion-induced compression maintains water at a significantly higher effective density, which in the region of the density anomaly is associated with greater mobility [3]. Hence this mechanism significantly reduces the tendency to both structural arrest and nucleation.

We also note that at high temperatures, away from water diffusion anomaly, the mixture behaves as expected; therefore, it slows down upon increasing the concentration of the solutes with respect to the bulk at the same temperature.

To further characterize this effect, we refer again to Fig. 6 where we plot τ_α^{-1} versus C at each of the considered values of T . From the curves we can see that upon increasing the concentration of the solutes, at high temperatures the capability of water to diffuse appears to be decreasing as expected in a normal liquid, while at lower temperatures, the system appears to have a faster diffusion instead. This relates the diffusion anomaly of bulk water, namely, the anomalous increase of the diffusion upon increasing densities, to this same behavior obtained upon increasing the solute concentration. We also note that for an intermediate temperature a maximum develops, while for the lower temperatures we expect it to be at even higher concentrations, since ultimately water will have to restore the normal behavior, as it happens in the bulk.

IV. CONCLUSIONS

In this work, we studied the dynamical behavior of super-cooled water in solutions with magnesium perchlorate. These systems are of significant relevance for planetary science due to their potential existence in the Martian subsurface. We employed the TIP4P/2005 potential for water combined with the flexible extended Madrid-2019 for the ions (model A). This potential produces good results both for density and transport properties with respect to the experiments. By means of MD

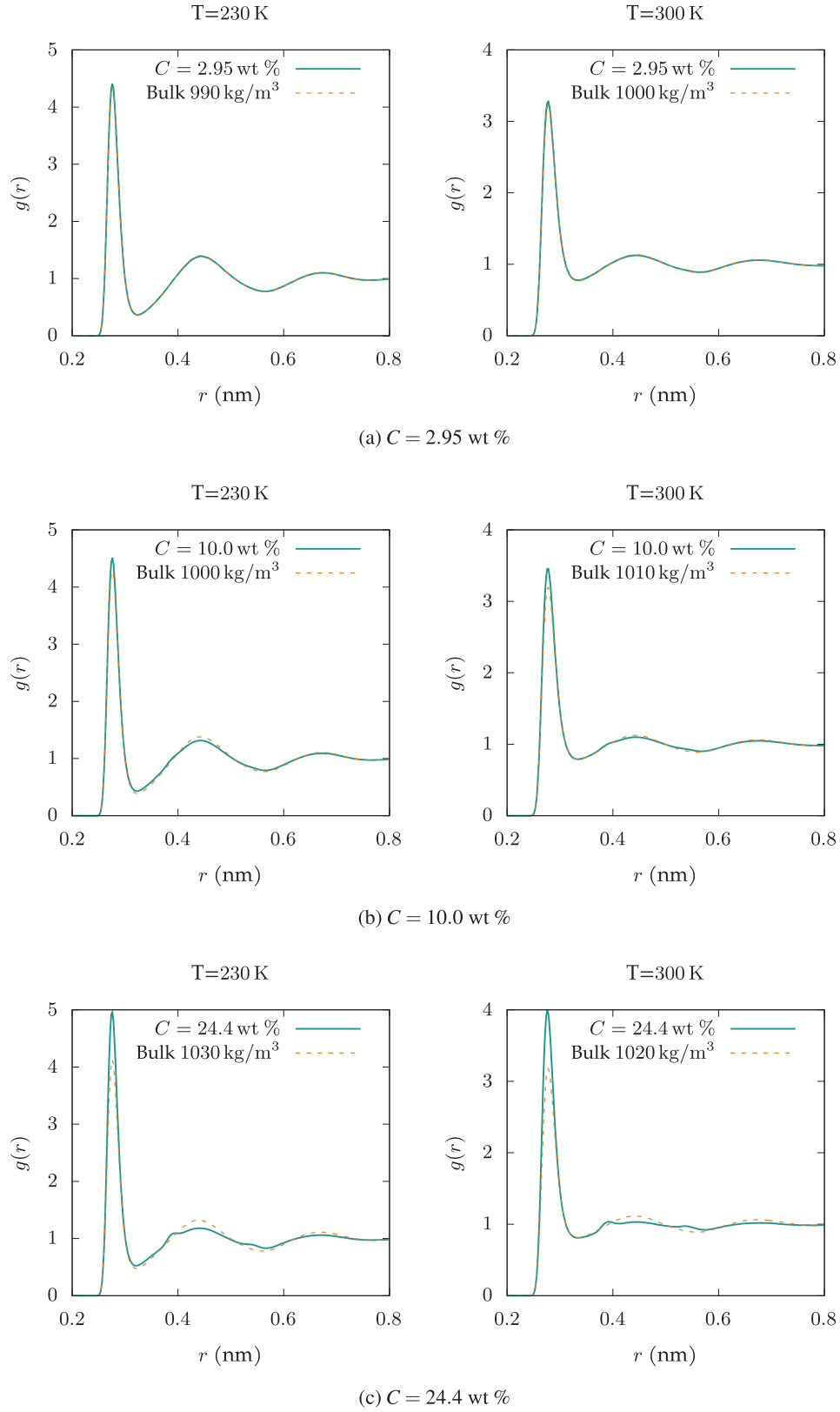


FIG. 8. Best match between the oxygen-oxygen radial distribution functions $g(r)$ of bulk water (dashed orange lines) and of water in magnesium perchlorate solutions (solid green lines). Comparisons are shown for $T = 300$ K and $T = 230$ K. The legend shows the bulk density whose RDF best matches the RDF of water in the solutions at $p = 5$ MPa for the concentration and temperatures specified in each panel.

simulations, we analyzed the relaxation dynamics of water molecules as a function of temperature and salt concentration at pressure and temperatures relevant for Martian studies with the aim to inquire on the possibility of the existence of water in the supercooled state on Mars.

Our analysis of the self-intermediate scattering functions reveals that the relaxation dynamics of water in these ionic solutions is similar to the bulk and it follows the two-step decay typical of glass formers. We confirmed the validity of the MCT and of the von Schweidler law in the mild supercooled regime in the solutions at all the concentrations investigated. We also identified the occurrence of a fragile-to-strong crossover at deep supercooling. This crossover marks the onset of a hopping-dominated dynamics.

A key finding of this study is the influence of perchlorate ions on the characteristic temperatures of these dynamical transitions. Upon increasing concentrations, we observed a downward shift in both the MCT temperature T_c and the FSC temperature T_{FSC} . This shift implies that the presence of ions extends the temperature range where water remains a supercooled liquid, effectively delaying the structural arrest associated with the glass transition.

Furthermore, we observed a counterintuitive acceleration of the dynamics in concentrated solutions compared to bulk water at low temperatures. We analyzed this behavior by studying the effective density of water and we showed that this acceleration is related to the diffusion anomaly of water. The insertion of ions effectively keeps water in a denser configuration and enhances its mobility, hindering formation of

the open tetrahedral network, which would be a precursor to ice nucleation.

In conclusion, the simultaneous downward shift of T_c and T_{FSC} , combined with the ion-induced local densification and water acceleration at lower temperatures, provides a dynamical and structural basis for the metastability of liquid water on Mars. These mechanisms suggest that aqueous solutions of magnesium perchlorate can remain in a metastable liquid phase at very low temperatures, offering an insight into the radar anomalies detected underneath the Martian South Polar Layered Deposits.

ACKNOWLEDGMENTS

This research was supported by PNRR-M4C2-I1.1-PRIN 2022-PE9-ARES – Assessing the Origin and Stability of Martian Subglacial Waters – Grant No. 2022W2BPCK, CUP F53D23001240006, funded by the European Union – NextGenerationEU and the Italian MUR.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

-
- [1] P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, Water: A tale of two liquids, *Chem. Rev.* **116**, 7463 (2016).
 - [2] P. Gallo and H. E. Stanley, Supercooled water reveals its secrets, *Science* **358**, 1543 (2017).
 - [3] P. G. Debenedetti, Supercooled and glassy water, *J. Phys.: Condens. Matter* **15**, R1669 (2003).
 - [4] C. A. Angell, Supercooled water, *Annu. Rev. Phys. Chem.* **34**, 593 (1983).
 - [5] P. Debenedetti, *Metastable Liquids: Concepts and Principles*, Physical Chemistry: Science and Engineering (Princeton University Press, Princeton, NJ, 1996).
 - [6] P. Gallo and M. Rovere, *Physics of Liquid Matter*, Soft and Biological Matter (Springer International Publishing, Berlin, 2021).
 - [7] R. Orosei, S. E. Lauro, E. Pettinelli, A. Cicchetti, M. Coradini, B. Cosciotti, F. D. Paolo, E. Flamini, E. Mattei, M. Pajola, F. Soldovieri, M. Cartacci, F. Cassenti, A. Frigeri, S. Giuppi, R. Martufi, A. Masdea, G. Mitri, C. Nenna, R. Noschese, *et al.*, Radar evidence of subglacial liquid water on Mars, *Science* **361**, 490 (2018).
 - [8] S. E. Lauro, E. Pettinelli, G. Caprarello, L. Guallini, A. P. Rossi, E. Mattei, B. Cosciotti, A. Cicchetti, F. Soldovieri, M. Cartacci, F. Di Paolo, R. Noschese, and R. Orosei, Multiple subglacial water bodies below the south pole of Mars unveiled by new MARSIS data, *Nat. Astron.* **5**, 63 (2021).
 - [9] R. J. Speedy, P. G. Debenedetti, R. S. Smith, C. Huang, and B. D. Kay, The evaporation rate, free energy, and entropy of amorphous water at 150 K, *J. Chem. Phys.* **105**, 240 (1996).
 - [10] O. Mishima and H. E. Stanley, The relationship between liquid, supercooled and glassy water, *Nature (London)* **396**, 329 (1998).
 - [11] K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, *et al.*, Maxima in the thermodynamic response and correlation functions of deeply supercooled water, *Science* **358**, 1589 (2017).
 - [12] A. Nilsson, Origin of the anomalous properties in supercooled water based on experimental probing inside “no-man’s land”, *J. Non-Cryst. Solids: X* **14**, 100095 (2022).
 - [13] M. Seidl, A. Fayter, J. N. Stern, G. Zifferer, and T. Loerting, Shrinking water’s no man’s land by lifting its low-temperature boundary, *Phys. Rev. B* **91**, 144201 (2015).
 - [14] W. Götze, *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory* (Oxford University Press, Oxford, UK, 2008).
 - [15] P. Gallo, F. Sciortino, P. Tartaglia, and S.-H. Chen, Slow dynamics of water molecules in supercooled states, *Phys. Rev. Lett.* **76**, 2730 (1996).

- [16] F. Sciortino, P. Gallo, P. Tartaglia, and S.-H. Chen, Supercooled water and the kinetic glass transition, *Phys. Rev. E* **54**, 6331 (1996).
- [17] R. Torre, P. Bartolini, and R. Righini, Structural relaxation in supercooled water by time-resolved spectroscopy, *Nature (London)* **428**, 296 (2004).
- [18] M. De Marzio, G. Camisasca, M. Rovere, and P. Gallo, Mode coupling theory and fragile to strong transition in supercooled TIP4P/2005 water, *J. Chem. Phys.* **144**, 074503 (2016).
- [19] M. De Marzio, G. Camisasca, M. Rovere, and P. Gallo, Microscopic origin of the fragile to strong crossover in supercooled water: The role of activated processes, *J. Chem. Phys.* **146**, 084502 (2017).
- [20] L. Lupi, B. Vázquez Ramírez, and P. Gallo, Dynamical crossover and its connection to the Widom line in supercooled TIP4P/ice water, *J. Chem. Phys.* **155**, 054502 (2021).
- [21] P. Gallo, M. Rovere, and S.-H. Chen, Water confined in MCM-41: A mode coupling theory analysis, *J. Phys.: Condens. Matter* **24**, 064109 (2012).
- [22] L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen, and C.-Y. Mou, Pressure dependence of fragile-to-strong transition and a possible second critical point in supercooled confined water, *Phys. Rev. Lett.* **95**, 117802 (2005).
- [23] F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, U. Wanderlingh, L. Liu, C.-Y. Mou, and S.-H. Chen, The fragile-to-strong dynamic crossover transition in confined water: Nuclear magnetic resonance results, *J. Chem. Phys.* **124**, 161102 (2006).
- [24] P. Gallo, M. Rovere, and E. Spohr, Supercooled confined water and the mode coupling crossover temperature, *Phys. Rev. Lett.* **85**, 4317 (2000).
- [25] P. Gallo, D. Corradini, and M. Rovere, Fragile to strong crossover at the Widom line in supercooled aqueous solutions of NaCl, *J. Chem. Phys.* **139**, 204503 (2013).
- [26] G. Camisasca, M. De Marzio, M. Rovere, and P. Gallo, High density liquid structure enhancement in glass forming aqueous solution of LiCl, *J. Chem. Phys.* **148**, 222829 (2018).
- [27] S.-H. Chen, L. Liu, E. Fratini, P. Baglioni, A. Faraone, and E. Mamontov, Observation of fragile-to-strong dynamic crossover in protein hydration water, *Proc. Natl. Acad. Sci. USA* **103**, 9012 (2006).
- [28] M. Lagi, X. Chu, C. Kim, F. Mallamace, P. Baglioni, and S.-H. Chen, The low-temperature dynamic crossover phenomenon in protein hydration water: Simulations vs experiments, *J. Phys. Chem. B* **112**, 1571 (2008).
- [29] G. Camisasca, M. De Marzio, D. Corradini, and P. Gallo, Two structural relaxations in protein hydration water and their dynamic crossovers, *J. Chem. Phys.* **145**, 044503 (2016).
- [30] A. Iorio, G. Camisasca, M. Rovere, and P. Gallo, Characterization of hydration water in supercooled water-trehalose solutions: The role of the hydrogen bonds network, *J. Chem. Phys.* **151**, 044507 (2019).
- [31] L. Lupi and P. Gallo, Glassy dynamics of water in TIP4P/ice aqueous solutions of trehalose in comparison with the bulk phase, *J. Chem. Phys.* **159**, 154504 (2023).
- [32] A. Iorio, L. Perin, and P. Gallo, Structure and slow dynamics of protein hydration water with cryopreserving DMSO and trehalose upon cooling, *J. Chem. Phys.* **160**, 244502 (2024).
- [33] L. Lupi and P. Gallo, Mode coupling behavior and fragile to strong transition of trehalose in a binary mixture with water upon supercooling, *J. Chem. Phys.* **160**, 244501 (2024).
- [34] L. Perin and P. Gallo, The effect of the cryoprotectant dimethyl sulfoxide on water upon supercooling: A molecular dynamics study, *J. Chem. Phys.* **163**, 214501 (2025).
- [35] P. Gallo and M. Rovere, Mode coupling and fragile to strong transition in supercooled TIP4P water, *J. Chem. Phys.* **137**, 164503 (2012).
- [36] M. De Marzio, G. Camisasca, M. Rovere, and P. Gallo, Fragile to strong crossover and Widom line in supercooled water: A comparative study, *Front. Phys.* **13**, 136103 (2018).
- [37] F. W. Starr, S. Harrington, F. Sciortino, and H. E. Stanley, Slow dynamics of water under pressure, *Phys. Rev. Lett.* **82**, 3629 (1999).
- [38] A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, Fragile-to-strong liquid transition in deeply supercooled confined water, *J. Chem. Phys.* **121**, 10843 (2004).
- [39] P. Gallo, M. Rovere, and S.-H. Chen, Dynamic crossover in supercooled confined water: Understanding bulk properties through confinement, *J. Phys. Chem. Lett.* **1**, 729 (2010).
- [40] R. Tyburski, M. Shin, S. You, K. Nam, M. Soldemo, A. Girelli, M. Bin, S. Lee, I. Andronis, Y. Han, S. Jeong, R. A. Oggenfuss, R. Mankowsky, D. Babich, X. Liu, S. Zerdane, T. Katayama, H. Lemke, F. Perakis, A. Nilsson, *et al.*, Observation of a dynamic transition in bulk supercooled water, *Nat. Phys.* **22**, 21 (2026).
- [41] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Phase behaviour of metastable water, *Nature (London)* **360**, 324 (1992).
- [42] J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, Metastable liquid-liquid transition in a molecular model of water, *Nature (London)* **510**, 385 (2014).
- [43] Y. Liu, J. C. Palmer, A. Z. Panagiotopoulos, and P. G. Debenedetti, Liquid-liquid transition in ST2 water, *J. Chem. Phys.* **137**, 214505 (2012).
- [44] Y. Liu, A. Z. Panagiotopoulos, and P. G. Debenedetti, Low-temperature fluid-phase behavior of ST2 water, *J. Chem. Phys.* **131**, 104508 (2009).
- [45] F. Sciortino, I. Saika-Voivod, and P. H. Poole, Study of the ST2 model of water close to the liquid-liquid critical point, *Phys. Chem. Chem. Phys.* **13**, 19759 (2011).
- [46] T. A. Kesselring, E. Lascaris, G. Franzese, S. V. Buldyrev, H. J. Herrmann, and H. E. Stanley, Finite-size scaling investigation of the liquid-liquid critical point in ST2 water and its stability with respect to crystallization, *J. Chem. Phys.* **138**, 244506 (2013).
- [47] F. Smallenburg and F. Sciortino, Tuning the liquid-liquid transition by modulating the hydrogen-bond angular flexibility in a model for water, *Phys. Rev. Lett.* **115**, 015701 (2015).
- [48] P. Gallo and F. Sciortino, Ising universality class for the liquid-liquid critical point of a one component fluid: A finite-size scaling test, *Phys. Rev. Lett.* **109**, 177801 (2012).
- [49] P. G. Debenedetti, F. Sciortino, and G. H. Zerbe, Second critical point in two realistic models of water, *Science* **369**, 289 (2020).
- [50] J. Weis, F. Sciortino, A. Z. Panagiotopoulos, and P. G. Debenedetti, Liquid-liquid criticality in the wail water model, *J. Chem. Phys.* **157**, 024502 (2022).

- [51] Y. Li, J. Li, and F. Wang, Liquid–liquid transition in supercooled water suggested by microsecond simulations, *Proc. Natl. Acad. Sci. USA* **110**, 12209 (2013).
- [52] R. Weldon and F. Wang, Water potential from adaptive force matching for ice and liquid with revised dispersion predicts supercooled liquid anomalies in good agreement with two independent experimental fits, *J. Phys. Chem. B* **128**, 3398 (2024).
- [53] F. Sciortino, Y. Zhai, S. L. Bore, and F. Paesani, Constraints on the location of the liquid–liquid critical point in water, *Nat. Phys.* **21**, 480 (2025).
- [54] O. Mishima and H. E. Stanley, Decompression-induced melting of ice IV and the liquid–liquid transition in water, *Nature (London)* **392**, 164 (1998).
- [55] K. Winkel, E. Mayer, and T. Loerting, Equilibrated high-density amorphous ice and its first-order transition to the low-density form, *J. Phys. Chem. B* **115**, 14141 (2011).
- [56] S. Woutersen, B. Ensing, M. Hilbers, Z. Zhao, and C. A. Angell, A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition, *Science* **359**, 1127 (2018).
- [57] K. H. Kim, K. Amann-Winkel, N. Giovambattista, A. Späh, F. Perakis, H. Pathak, M. L. Parada, C. Yang, D. Mariedahl, T. Eklund, T. J. Lane, S. You, S. Jeong, M. Weston, J. H. Lee, I. Eom, M. Kim, J. Park, S. H. Chun, P. H. Poole, *et al.*, Experimental observation of the liquid-liquid transition in bulk supercooled water under pressure, *Science* **370**, 978 (2020).
- [58] S. You *et al.*, Experimental evidence of a liquid-liquid critical point in supercooled water, *Science* **391**, 1387 (2026).
- [59] D. G. Archer and R. W. Carter, Thermodynamic properties of the NaCl + H₂O system. 4. Heat capacities of H₂O and NaCl(aq) in cold-stable and supercooled states, *J. Phys. Chem. B* **104**, 8563 (2000).
- [60] D. Corradini, M. Rovere, and P. Gallo, A route to explain water anomalies from results on an aqueous solution of salt, *J. Chem. Phys.* **132**, 134508 (2010).
- [61] D. Corradini, Z. Su, H. E. Stanley, and P. Gallo, A molecular dynamics study of the equation of state and the structure of supercooled aqueous solutions of methanol, *J. Chem. Phys.* **137**, 184503 (2012).
- [62] L.-A. Näslund, D. C. Edwards, P. Wernet, U. Bergmann, H. Ogasawara, L. G. M. Pettersson, S. Myneni, and A. Nilsson, X-ray absorption spectroscopy study of the hydrogen bond network in the bulk water of aqueous solutions, *J. Phys. Chem. A* **109**, 5995 (2005).
- [63] D. Corradini, M. Rovere, and P. Gallo, Structural properties of high and low density water in a supercooled aqueous solution of salt, *J. Phys. Chem. B* **115**, 1461 (2011).
- [64] D. Corradini and P. Gallo, Liquid–liquid coexistence in NaCl aqueous solutions: A simulation study of concentration effects, *J. Phys. Chem. B* **115**, 14161 (2011).
- [65] I. Waluyo, D. Nordlund, U. Bergmann, D. Schlesinger, L. G. M. Pettersson, and A. Nilsson, A different view of structure-making and structure-breaking in alkali halide aqueous solutions through x-ray absorption spectroscopy, *J. Chem. Phys.* **140**, 244506 (2014).
- [66] L. Perin and P. Gallo, Phase diagram of aqueous solutions of LiCl: A study of concentration effects on the anomalies of water, *J. Phys. Chem. B* **127**, 4613 (2023).
- [67] L. Perin and P. Gallo, Thermodynamics, phase diagram, structure and anomalies of supercooled aqueous solutions of trehalose: A molecular dynamics study, *J. Mol. Liq.* **414**, 126089 (2024).
- [68] C. Calvagna, A. Lapini, A. Taschin, S. Fanetti, M. Pagliai, P. Bartolini, R. Bini, R. Righini, and R. Torre, Modification of local and collective dynamics of water in perchlorate solution, induced by pressure and concentration, *J. Mol. Liq.* **337**, 116273 (2021).
- [69] P. La Francesca and P. Gallo, Supercooled solutions of sodium perchlorate in TIP4P/2005 water: The effect of Martian solutes on thermodynamics and structure, *J. Chem. Phys.* **159**, 124501 (2023).
- [70] P. La Francesca and P. Gallo, Phase diagram and structure of TIP4P/2005 water and magnesium perchlorate: A molecular dynamic study of Martian aqueous solutions, *J. Mol. Liq.* **417**, 126673 (2025).
- [71] P. La Francesca and P. Gallo, Molecular dynamics simulations of supercooled aqueous solutions of calcium perchlorate: Thermodynamics and structure of Martian solutes in TIP4P/2005 water, *J. Phys. Chem. B* **129**, 8776 (2025).
- [72] M. Allen, D. Tildesley, and D. Tildesley, *Computer Simulation of Liquids*, Oxford Science Publications (Oxford University Press, Oxford, UK, 2017).
- [73] B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl, Gromacs 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation, *J. Chem. Theory Comput.* **4**, 435 (2008).
- [74] H. J. Berendsen, D. van der Spoel, and R. van Drunen, Gromacs: A message-passing parallel molecular dynamics implementation, *Comput. Phys. Commun.* **91**, 43 (1995).
- [75] J. L. Abascal and C. Vega, A general purpose model for the condensed phases of water: TIP4P/2005, *J. Chem. Phys.* **123**, 234505 (2005).
- [76] I. M. Zeron, J. L. F. Abascal, and C. Vega, A force field of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl[−], and SO₄^{2−} in aqueous solution based on the TIP4P/2005 water model and scaled charges for the ions, *J. Chem. Phys.* **151**, 134504 (2019).
- [77] S. Blazquez, J. Troncoso, P. La Francesca, P. Gallo, M. Conde, and C. Vega, Extending the Madrid-2019 force field to the perchlorate anion: Role of charge distribution and validation with experiments on Mars-relevant aqueous solutions, *J. Mol. Liq.* **435**, 128035 (2025).
- [78] B. Hess, P-LINCS: A parallel linear constraint solver for molecular simulation, *J. Chem. Theory Comput.* **4**, 116 (2008).
- [79] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, A smooth particle mesh Ewald method, *J. Chem. Phys.* **103**, 8577 (1995).
- [80] G. Bussi, D. Donadio, and M. Parrinello, Canonical sampling through velocity rescaling, *J. Chem. Phys.* **126**, 014101 (2007).
- [81] M. Parrinello and A. Rahman, Crystal structure and pair potentials: A molecular-dynamics study, *Phys. Rev. Lett.* **45**, 1196 (1980).
- [82] M. Parrinello and A. Rahman, Polymorphic transitions in single crystals: A new molecular dynamics method, *J. Appl. Phys.* **52**, 7182 (1981).
- [83] S. E. Lauro, E. Pettinelli, G. Caprarello, J. Baniamerian, E. Mattei, B. Cosciotti, D. E. Stillman, K. M. Primm, F. Soldovieri, and R. Orosei, Using MARSIS signal attenuation to assess the presence of South Polar Layered Deposit subglacial brines, *Nat. Commun.* **13**, 5686 (2022).

- [84] G. Franzese and H. E. Stanley, The Widom line of supercooled water, *J. Phys.: Condens. Matter* **19**, 205126 (2007).
- [85] L. Xu, P. Kumar, S. V. Buldyrev, S.-H. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley, Relation between the Widom line and the dynamic crossover in systems with a liquid–liquid phase transition, *Proc. Natl. Acad. Sci. USA* **102**, 16558 (2005).
- [86] J. L. Abascal and C. Vega, Widom line and the liquid–liquid critical point for the TIP4P/2005 water model, *J. Chem. Phys.* **133**, 234502 (2010).
- [87] J. R. Errington and P. G. Debenedetti, Relationship between structural order and the anomalies of liquid water, *Nature (London)* **409**, 318 (2001).