

Reorientational dynamics of water in aqueous ionic solutions at supercritical conditions: A computer simulation study

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Abstract

We present results of a computer simulation study on the reorientational dynamics of water molecules in aqueous ionic solutions at supercritical conditions. We carried out molecular dynamics simulations along the isotherm $T=650$ K and densities ranging from $\rho=0.7$ g cm⁻³ down to $\rho=0.05$ g cm⁻³. We adopted the SPC/E water model. The ionic species included Na⁺ and Cl⁻ ions. Our attention has been focused on the reorientational dynamics of the solvation shell molecules. Reorientational correlation times are reported and compared with those corresponding to pure water at the same thermodynamic conditions. We find that the influence of the ions goes beyond the first solvation shell and significantly affects the motion of the molecules lying in the second solvation shell. This differs with earlier studies of aqueous ionic solutions at room temperature.

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1. Introduction

Liquid water is a peculiar substance since it has extraordinary microscopic properties uncommon to the majority of liquids. There is general agreement that the main responsibility for those properties has to be charged to the presence in water of a special type of molecular bond called “hydrogen-bond” (HB) [1,2]. Hence, hydrogen-bond distributions and the rates of HB breaking and reformation drive microscopic water dynamics in the sub-picosecond time scale. When turning to supercritical conditions we can force water to change some of its properties, because the density can be experimentally controlled by pressure and temperature changes, varying the microscopic ambient in between liquid-like and gas-like environments. In such landscape, big variations of the static dielectric constant happen. It is reduced from ~ 80 at ambient conditions to only ~ 6 in a typical supercritical regime. The behavior of water is then closer to a non-polar solvent, instead of its polar solvent characteristics at room temperature. This

fact produces the well-known ability of supercritical water to dissolve non-polar organic reactives and also explains the existence of separated contact ion pairs in a low-density ambient, turning to dissociated ions when density is increased.

Ionic aqueous solutions are ubiquitous in nature and play a central role in environmental and industrial processes like microbiology [3], oxidation of chemical and biochemical wastes [4], metal corrosion [5] or electrode processes [6], to mention a few examples. The presence of ionic species can produce important perturbations of both the structure and dynamics of water through changes in the behavior of the HB network. Further, the mechanisms of aqueous ion solvation are arguably called to play a key role in the understanding of proton and charge transfer reactions. From the experimental side, electric field [7], calorimetric [8] conductivity [9], infrared and Raman spectroscopic measurements [10–12], extended X-ray absorption fine structure spectroscopy [13,14], neutron diffraction with isotopic substitution [15–17] and, more recently, nonlinear femtosecond spectroscopy [18] are able to reveal indirect information on dynamics of aqueous ionic solvation. On the theoretical side, integral equation calculations and numerical studies based on computer simulations report

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valuable information on structural and dynamical properties of ionic aqueous solutions at ambient [19–21], high-temperature [22–26] and supercritical states [27–35]. As the “third way”, computer simulation has emerged as a powerful tool for investigating the microscopic properties of liquids and liquid solutions. Computer simulations can provide experimentally inaccessible information which may be very useful for a deep understanding of these systems at the molecular level. This information is also very helpful for interpreting experimental data such as those resulting from spectroscopic experiments. The wide use of the Monte Carlo and molecular dynamics (MD) techniques has allowed the investigation of hydrogen-bond dynamics through the calculation of HB lifetimes in bulk water at different thermodynamic conditions [36–40] and, more recently, in aqueous electrolyte solutions at room temperature [20,41]. However, the studies related to HB and reorientational dynamics in supercritical ionic aqueous solutions are scarce in the literature.

In this contribution we report the results of an MD study on the reorientational dynamics of water molecules in aqueous ionic solutions at supercritical conditions. The outline of this paper is as follows. Computational details of the MD simulations are given in Section 2. The structure and residence times of water molecules around the ionic species are determined in Section 3. The orientations of solvation shell molecules are analyzed in Section 4. Section 5 is devoted to the reorientational dynamic properties and conclusions are given in Section 6.

2. Computational details

We carried out MD simulations on a system containing one ion, either Na^+ or Cl^- and 255 water molecules with periodic boundary conditions. In each case, the temperature of the system was fixed at $T=650$ K and the size of the cubic box was chosen to give a solvent density interval ranging from $\rho=0.7$ and 0.05 g cm^{-3} . The SPC/E model was adopted for water–water interactions [42]. This is a three-site water model which has been widely used for pure water as well as for aqueous ionic solutions. Ion–water forces were modeled by means of a sum of pairwise additive Coulombic and 6–12 Lennard-Jones site–site potentials. The Lorentz-Berthelot mixing rules, i.e. $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ were assumed. We adopted the set of ion Lennard-Jones parameters derived by Dang [43]. All the potential parameters are collected in Table 1.

In order to carry out the simulations, we employed the integration algorithm of Berendsen et al. [44] with a time step of 0.002 ps and a thermal bath coupling parameter of 0.2 ps.

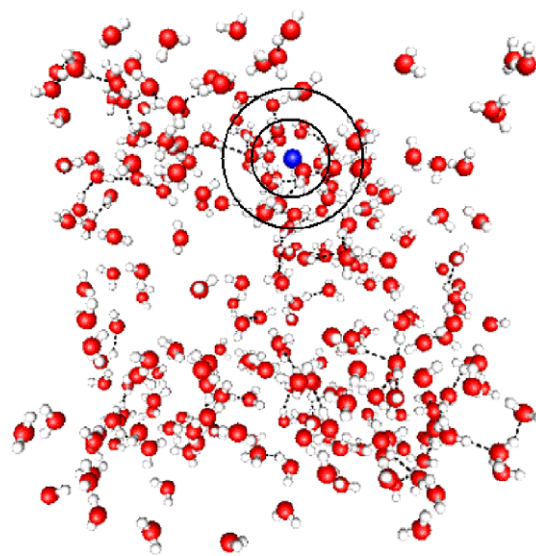


Fig. 1. Snapshot of an MD configuration of one Na^+ ion (in blue) in SPC/E water at $T=650$ K and $\rho=0.3$ g cm^{-3} . The circles correspond to the 1st and 2nd solvation shells (see the text). The dashed lines indicate H-bonded molecules. Oxygens (red), hydrogens (white).

Short-ranged forces were truncated at half the box length and the Ewald summation method with conducting boundary conditions [45] was applied to account for long-ranged Coulomb interactions. Each run consisted of an initial equilibration period of 50 ps and a production period of 500 ps to collect statistically meaningful properties. A snapshot of a typical MD configuration is depicted in Fig. 1. The circles correspond to the 1st and 2nd solvation shells. The radii of the shells were determined from the minima of the ion–oxygen radial distribution functions (see next section). The dashed lines indicate H-bonded molecules. A detailed analysis of the H-bond dynamics will be reported elsewhere [46].

3. Ion–water structure and residence times

The ion–oxygen radial distribution functions $g_{\text{IO}}(r)$ obtained for both Na^+ and Cl^- at different solvent densities are shown in Fig. 2. The position of the first and second minima of these functions allowed us to determine the radii R_{shell} of the first and second solvation shells, respectively. First minima are well resolved for Na^+ whereas they are rather unclear for Cl^- . In all cases, the second minima are ambiguous. We observe that both first and second solvation shells are located at nearly the same positions for all densities in the case of Na^+ . Conversely, for Cl^- the position of the first minimum in the $g_{\text{IO}}(r)$ tends to move to larger values as density decreases. These two features were also observed by Rasaiah et al. [31] at 683 K and densities ranging from 1 to 0.2 g cm^{-3} . The assumed R_{shell} values and the mean number of molecules within a given shell n_{shell} are listed in Table 2. The number of water molecules is reduced as density decreases in both shells, as expected. In the first shell, the changes are only up to 1 molecule, considering the two extremal densities. The largest variations are found in the

Table 1
Interaction potential parameters

Ion/atom	ϵ (kcal/mol)	σ (Å)	q (e)	Ref.
Na^+	0.100	2.584	+1.0	[43]
Cl^-	0.100	4.401	−1.0	[43]
Oxygen	0.155	3.166	−0.8476	[42]
Hydrogen			+0.4236	[42]

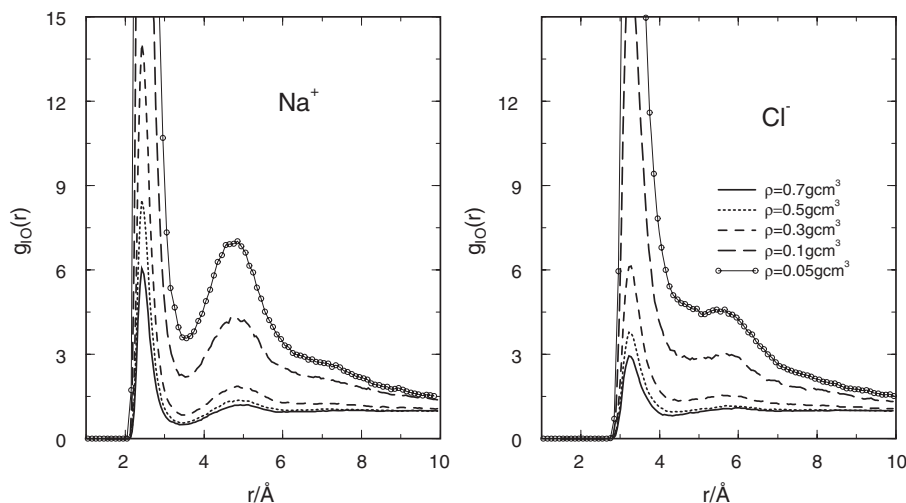


Fig. 2. Ion–oxygen radial distribution functions for Na^+ (left) and Cl^- (right) in water at $T=650$ K and different solvent densities.

second shell, which has populations near three times those of the first shell at 0.7 g cm^{-3} for the two ionic species. However, the mean number n_{shell} is gradually reduced for decreasing density. In the lowest density case, we observe that the populations of both the first and second coordination shells are basically the same. This is an indication of the range of the ionic attractive forces, which are able to maintain the basic structure of the first ionic shells, regardless of the density considered. Such attraction is clearly reduced in the second shell, probably due to the screening role played by the water molecules in the first shell. In parallel, we must keep in mind the destruction, in supercritical ambient, of the HB network existing at room conditions. At low densities, where most of the HB structure is lost [38], water molecules show a behavior much closer to that of a gas.

In the context of studies concerning ion–water interactions, structure and dynamics of hydration shells are of central importance. Several studies of solvent exchange within hydration shells have been recently published [47–49]. In particular, solvent exchange dynamics is deeply connected with the computation of residence times on solvation shells reported in the present work. The residence time of water molecules in given solvation shells was evaluated by using the procedure

described in Ref. [50]. A brief summary of the method is as follows: during the simulations, we computed the function $n(t)$ which is defined as the number of molecules that having initially been in a given solvation shell remain there after a time t , independently whether they have been outside for any period smaller than t . The initial value $n(0)$ is just n_{shell} . The residence time in the solvation shell τ_{res} is then determined as the time integral

$$\tau_{\text{res}} = \int_0^{\infty} \frac{n(t)}{n(0)} dt. \quad (1)$$

The results for τ_{res} are presented in Fig. 3. A primary comparison between residence times at ambient [47] and supercritical ambients (this work) reveal that the former are about a factor of 3 to 7 times longer than those at supercritical conditions. In the present case, residence times in the first solvation shells are higher than those in the second solvation shells. The differences are more important for Na^+ than for Cl^- . For both ions, in the case of the first solvation shell molecules, τ_{res} systematically increases as ρ diminishes. The residence

Table 2
Radius of the solvation shells, mean number of molecules within a given shell, and mean orientation of the solvation shell molecules

Ion	ρ (g cm^{-3})	R_{shell} (Å)		n_{shell}		$\langle \theta \rangle$ (deg)	
		1st shell	2nd shell	1st shell	2nd shell	1st shell	2nd shell
Na^+	0.7	3.5	6.0	6	17	139 (23)	106 (38)
	0.5	3.5	6.0	5.5	13.5	142 (22)	111 (37)
	0.3	3.5	6.0	5.5	11	143 (21)	115 (35)
	0.1	3.5	6.0	5.0	8.0	145 (19)	122 (33)
	0.05	3.5	6.0	5.0	6.0	147 (18)	129 (29)
Cl^-	0.7	4.2	7.0	7.5	26	53 (23)	78 (38)
	0.5	4.5	7.0	8	19	53 (24)	75 (38)
	0.3	4.5	7.0	7.5	15	51 (23)	71 (37)
	0.1	4.6	7.2	7.0	10.5	48 (22)	65 (35)
	0.05	5.0	7.5	7.0	7.0	47 (22)	59 (33)

Quantities in parenthesis are standard deviations.

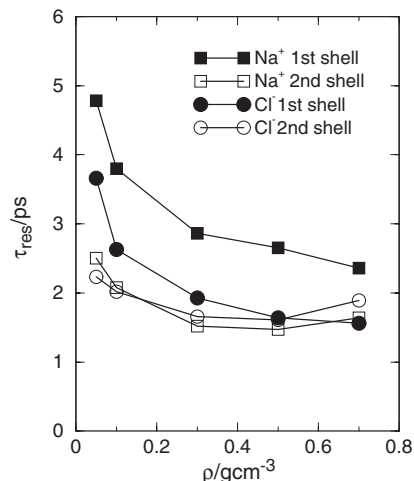


Fig. 3. Residence times τ_{res} for the first and second solvation shell molecules of Na^+ and Cl^- in water at $T=650$ K as a function of solvent density.

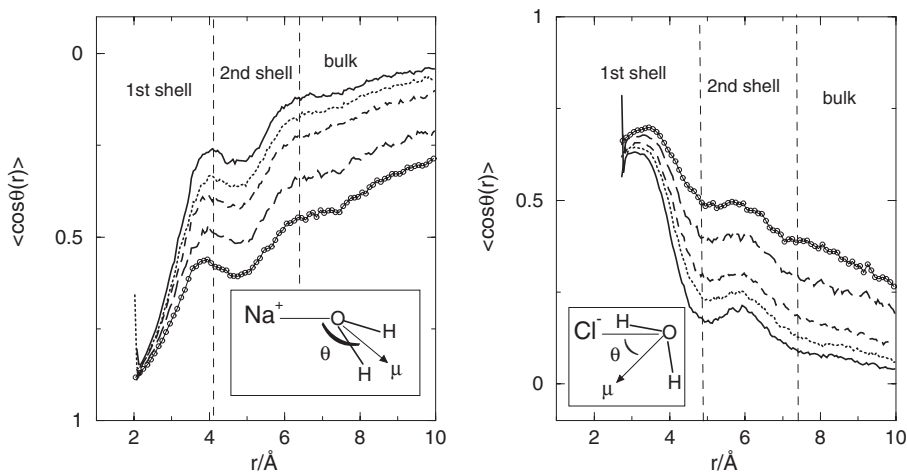


Fig. 4. Mean value of $\cos \theta$ as a function of ion–oxygen distance for Na^+ (left) and Cl^- (right) in water at $T=650$ K and different solvent densities. The different curves are as in Fig. 2. The most probable orientations of molecules around each ion are also drawn.

time of water molecules in the second solvation shell is weakly dependent on solvent density and has a shallow minimum around $\rho=0.4$ g cm^{-3} for both Na^+ and Cl^- . The behavior in the first shell seems to be related with the stability provided by the close presence of the ionic species. Conversely, for water in the second shells ions are quite far apart (around 6 \AA) and the attractive forces are significantly reduced leading to shorter residence times.

4. Orientation of the molecules

The orientation of the water molecules in the solvation shells was analyzed by computing the angle θ between the dipole moment of the water molecule and the ion–oxygen displacement vector. The mean value of $\cos \theta$ as a function of the ion–solvent distance $\langle \cos \theta(r) \rangle$ and the most probable orientation of water molecules around each ion are shown in

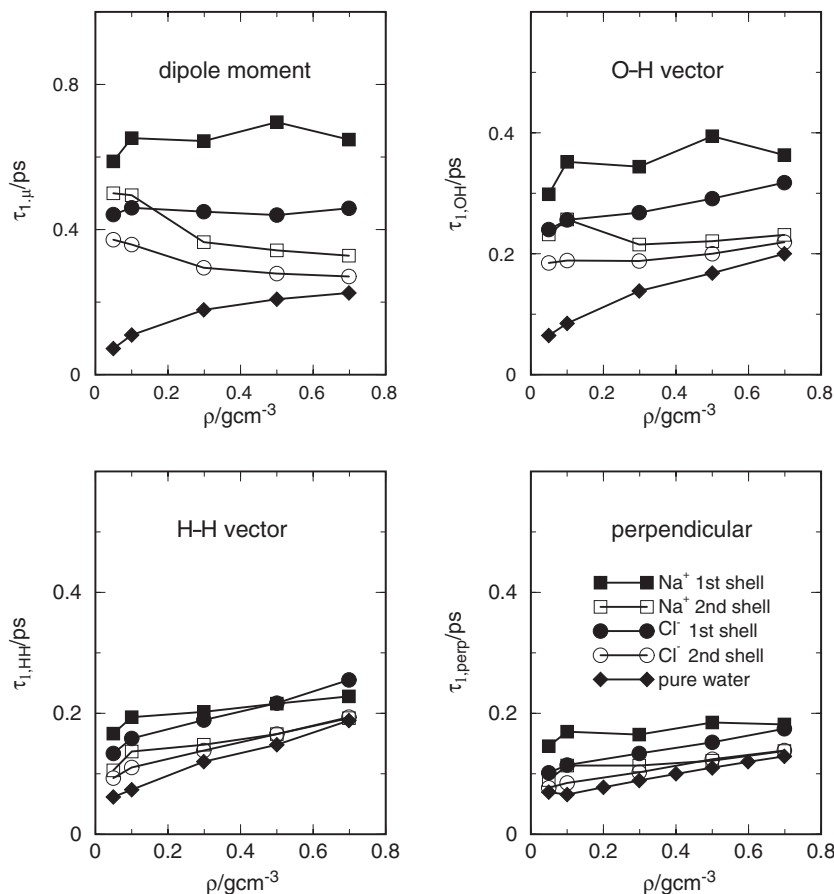


Fig. 5. Reorientational correlation times $\tau_{1,\alpha}$ along different molecular directions for the first and second solvation shell molecules of Na^+ and Cl^- in water at $T=650$ K as a function of solvent density. The pure water values were taken from Refs. [53] and [54].

Fig. 4. In the vicinity of Na^+ , water molecules exhibit a trigonal orientation with θ close to 180° . In the case of Cl^- , water molecules orientate with one of the hydrogens pointing towards the ion so that θ is nearly 50° . As expected, the influence of the ions on the orientation of the water molecules diminishes as the distance increases. At high density, that influence is of little importance beyond the first solvation shell. Similar findings were observed for aqueous ionic solutions at ambient conditions [51]. Orientational ordering becomes stronger as ρ diminishes and progressively extends to the second solvation shell as well as to the bulk region. For the sake of completeness, the mean orientation $\langle\theta\rangle$ around each ion for both the first and second solvation shell molecules is listed in Table 2 for all the analyzed solvent densities. The fluctuations of $\langle\theta\rangle$ are larger in the second solvation shells, indicating a greater degree of delocalization.

5. Reorientational correlation times

Molecular reorientational motions in liquids are usually analyzed through the time correlation functions:

$$C_{l,\alpha}(t) = \langle P_l(\vec{u}_\alpha(t) \cdot \vec{u}_\alpha(0)) \rangle, \quad (2)$$

where P_l refers to the l th Legendre polynomial and \vec{u}_α is a unit vector along a given direction. We calculated $C_{1,\alpha}(t)$ and

$C_{2,\alpha}(t)$ for four different \vec{u}_α unit vectors: a unit vector \vec{u}_μ along the molecular dipole moment direction, a unit vector \vec{u}_{HH} along the H–H direction, a unit vector \vec{u}_{OH} along the O–H direction and a unit vector $\vec{u}_\perp = \vec{u}_\mu \times \vec{u}_{\text{HH}}$ perpendicular to the molecular plane. $C_{1,\mu}(t)$ and $C_{2,\text{OH}}(t)$ are related to dielectric and NMR relaxation measurements, respectively (see, for instance, Ref. [52]).

In order to make a quantitative analysis of the rotational dynamics we evaluated the reorientational correlation times $\tau_{l,\alpha}$ for all the analyzed molecular directions as the time integrals:

$$\tau_{l,\alpha} = \int_0^\infty C_{l,\alpha}(t) dt. \quad (3)$$

The resulting values for $\tau_{1,\alpha}$ are displayed in Fig. 5 and those for $\tau_{2,\alpha}$ in Fig. 6. The molecular reorientational times obtained in a previous study of pure water [54] at the same thermodynamic conditions are also depicted. Before entering into the discussion of the results, we would like to point out that the values of $\tau_{l,\alpha}$ are one order of magnitude lower than the residence times shown in Fig. 3. This suggests that the breakdown of the solvation shells involves more complicated mechanisms than simple molecular reorientations. In addition, we observe that $\tau_{1,\alpha} > \tau_{2,\alpha}$ in about a factor of two.

A first remarkable fact is the change in all reorientational times when we compare them at ambient [41,55] and

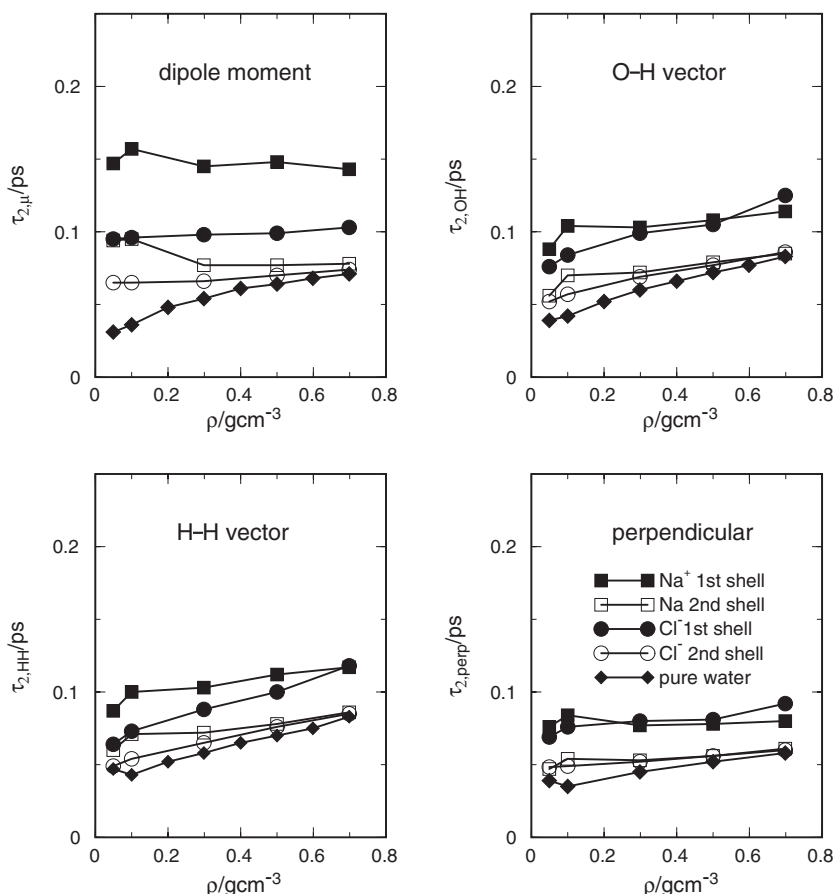


Fig. 6. Reorientational correlation times $\tau_{2,\alpha}$ along different molecular directions for the first and second solvation shell molecules of Na^+ and Cl^- in water at $T=650$ K as a function of solvent density. The pure water values were taken from Refs. [53] and [54].

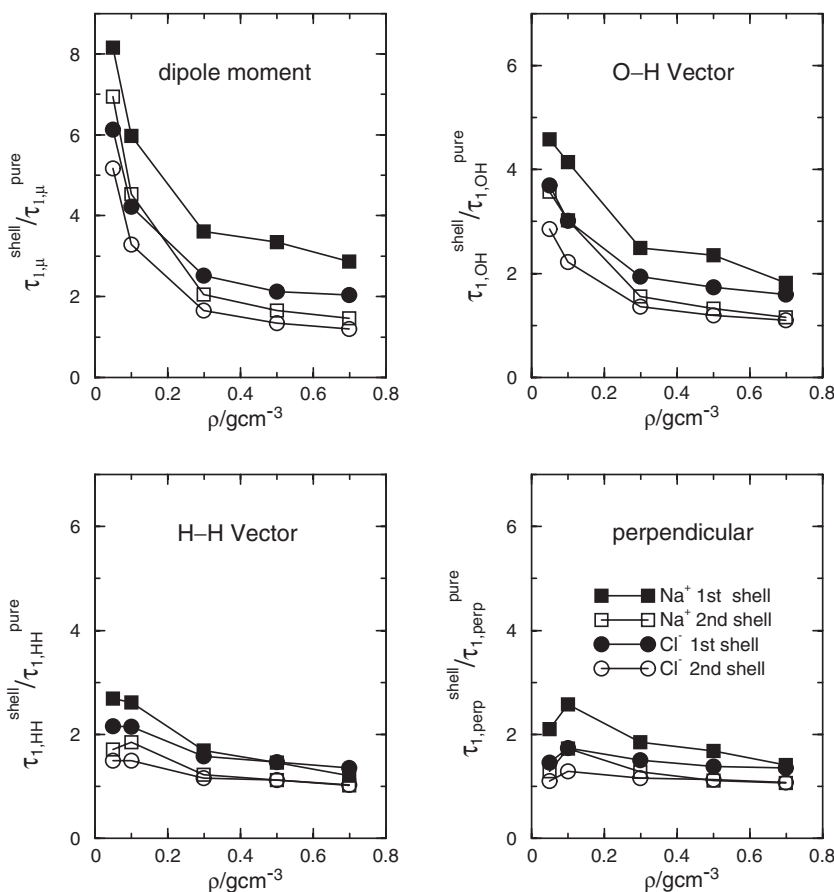


Fig. 7. Ratio $\tau_{1,\alpha}^{\text{shell}}/\tau_{1,\alpha}^{\text{pure}}$ between the reorientational correlation times for the first and second solvation shell molecules of Na⁺ and Cl⁻ and pure water at $T=650$ K and different solvent densities.

supercritical conditions, being in the order of 10 ps at 298 K and in the order of 1 ps at 650 K. In the case of supercritical water ionic solutions, the general trends are: first, the two reorientational times $\tau_{1,\alpha}$ are, in general, larger than their analogous counterparts for pure water at the same thermodynamic conditions [54]; second, with only a few exceptions, times of water reorientation around sodium are longer than those around chlorine and third, water molecules located in the first ionic solvation shells present, for each ion, longer τ_1 and τ_2 than those of water in the second ionic shells.

The study of the ratio $\tau_{1,\alpha}^{\text{shell}}/\tau_{1,\alpha}^{\text{pure}}$ provides us with a direct way to investigate the influence of ionic species in reorientational correlation times. The results are presented in Figs. 7 and 8. Ionic influence is remarkably important at low densities and for water molecules living in the first ionic shells. The latter fact is in good agreement with the findings of Fig. 4, where the angular distributions show sharp profiles mainly for water nearby the ionic species. In both figures, we observe that the ratio $\tau_{1,\alpha}^{\text{shell}}/\tau_{1,\alpha}^{\text{pure}}$ produces larger values in the case of Na⁺ than for Cl⁻. The values are particularly remarkable in the cases of dipole moment and OH vector reorientations.

Those results confirm the dominance of the ion–water forces over water–water interactions when few water molecules are present and the reduction of this effect as density increases. In pure water, the largest τ were observed at low densities as well. This was assigned to the breakdown of the

HB network as density is reduced, allowing water to “spin” in a faster way. In the present case, the ionic presence seems to partially prevent such quick rotational motions. This is consistent with the fact that reorientational times for HH and perpendicular vectors are much closer in ionic and pure water environments, giving an indication of a smaller influence of ionic species along directions nearly orthogonal to the quasi-linear direction indicated by water–water HB.

Finally, we would like to emphasize an interesting feature observed in Fig. 8. It is associated with the smooth maxima obtained around 0.1 g cm^{-3} for all cases, excepting the molecular dipole moment. In our opinion, these maxima have to be related with corresponding minima at nearly the same densities in the reorientational times τ_2 for pure water (Fig. 6 of Ref. [54]).

6. Summary

To conclude this paper, we should point out again the novelty of the calculations reported here. This is one of the first publications including results on molecular reorientational dynamics of water in ionic supercritical environments. We have considered two ionic species (Na⁺ and Cl⁻) and a range of densities between 0.7 and 0.05 g cm^{-3} at a supercritical isotherm of 650 K. The structure of water has been analyzed up to the second ionic solvation shell. We found very well defined

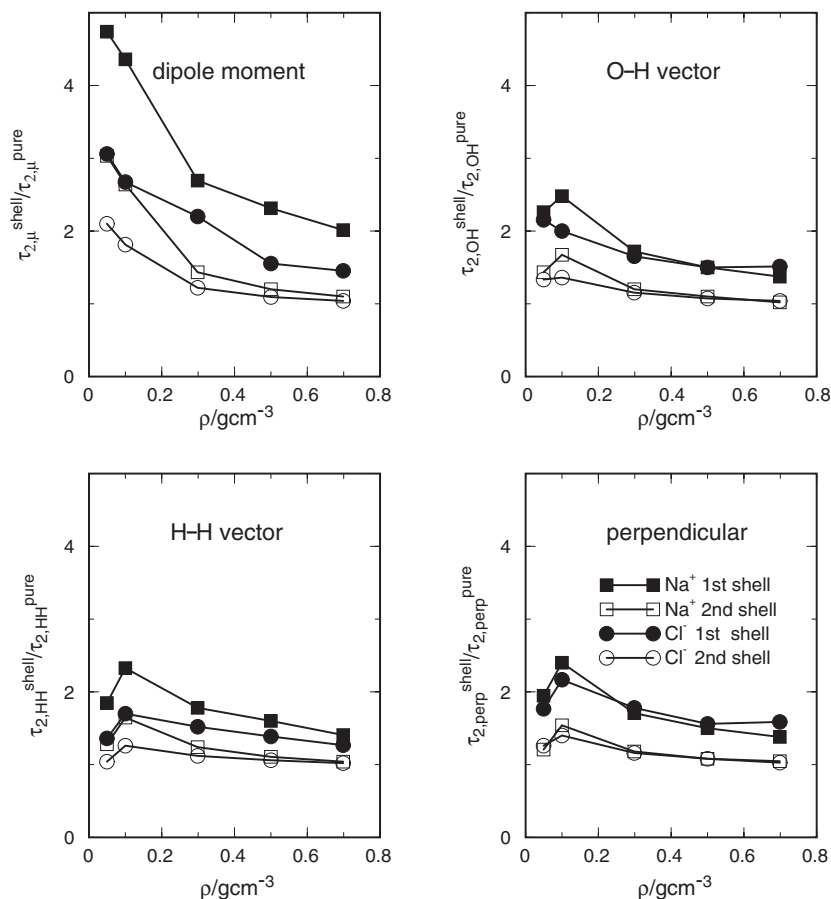


Fig. 8. Ratio $\tau_{2,x}^{\text{shell}}/\tau_{2,x}^{\text{pure}}$ between the reorientational correlation times for the first and second solvation shell molecules of Na⁺ and Cl⁻ and pure water at $T=650$ K and different solvent densities.

first shells, whereas the limits for the second shells were rather loose. These findings are deeply connected with the stability of water populations in each shell. Residence times of water molecules in the first ionic shells are significantly longer than those of the second shells, although the differences are more important at low densities. From angular distributions, we observed marked orientations especially in the case of water nearby the ionic species. Such ordering is gradually destroyed as density increases. The analysis of the mean time required for a water molecule to change the orientation of several particularly defined vectors have indicated slower motions in the case of water molecules nearby the ions, especially in the case of directions closely related with those connected to the HB network.

Acknowledgments

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