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Ion hydration and structural properties of water in aqueous solutions at normal and supercooled conditions: a test of the structure making and breaking concept

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We study with the method of molecular dynamics simulation the structural properties of aqueous solutions of NaCl, KCl and KF salts at ambient conditions and upon supercooling at constant pressure. The calculations are performed at increasing concentration of the salt starting from $c = 0.67$ mol kg^{-1} up to 3.96 mol kg^{-1}. We investigate the modifications of the hydration shells and the changes in the water structure induced by the presence of the ions. The oxygen–oxygen structure is strongly dependent on the ionic concentration while it is almost independent from the cation. The hydrogen bonding is preserved at all concentrations and temperatures. The main effect of increasing the ionic concentration is the tendency of the water structure to assume the high density liquid form predicted for pure water upon supercooling. An important consequence of our analysis is that the concept of an ion as a structure maker or a structure breaker must be revisited to take into account the other ionic species, the ionic concentration and more generally the thermodynamic conditions of the solutions.

1 Introduction

Aqueous solutions of salts are systems of great interest in many fields of chemistry, biochemistry, physics and chemical engineering. Different phenomena taking place in electrolyte solutions,[1,2] in proteins,[3–5] and in biological membranes[6] are related to the interactions between ions and water. At the microscopic level it is important to understand how the individual ions influence the structure of water and how the water molecules are arranged around the different types of cations and anions. For these reasons, ionic aqueous solutions have been the subject of several experimental[7–16] and computer simulation studies for a long time.[17–39]

In the old classification scheme related to the Hofmeister series,[3,40] anions and cations are ordered according to their properties of enhancing (structure makers) or weakening (structure breakers) the hydrogen bond (HB) network of water molecules.[41,42] The structure makers, also classified as kosmotropes, are considered to be strongly hydrated. They break the HB in the surrounding water molecules, in such a way that the rest of the water molecules can rearrange in an ordered hydration structure. On the contrary, structure breaking ions, also called chaotropes, interact weakly with the nearby

water molecules and induce a disordering in the tetrahedrally coordinated network of water.

The Hofmeister series is widely used in the interpretation of the properties of ionic solutions,[43] in recent years however this classification scheme has been challenged by a number of experimental studies.[15,16,44,45] It is argued that the classification scheme of the ions in terms of structure makers/breakers does not take into account the effects of the ion concentration and the thermodynamic conditions on the behaviour of the solutions. Evidences from experiments[16] and computer simulations[36] indicate that ions, regardless of the kind, perturb the water structure beyond the first hydration shell and that effect is similar to the application of pressure on pure water.

An important issue connected to phenomena occurring in aqueous solutions of salts appeared recently in the literature. It has been found that these systems are relevant in the study of the anomalous behaviour of water upon supercooling.[38]

On the basis of computer simulation results, the existence of a second critical point of water in the supercooled metastable liquid phase has been hypothesized since 1992.[46,47] This critical point would be at the end of a coexistence line between two phases called low density liquid (LDL) and high density liquid (HDL). LDL and HDL would come from the extension to higher temperatures (above 140 K) of the experimentally determined low density amorphous and high density amorphous phases of glassy water, among them there exist a first order transition.[48–51]

Since the publication of the first study, a number of experimental and computational investigations were performed to

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test the hypothesis of a liquid–liquid critical point (LLCP) against alternative interpretations of the anomalous behaviour of water upon supercooling.[52–60]

In settling the controversial issue about the existence of this second critical point the main difficulty is that experimental studies of the thermodynamic region of the HDL and LDL coexistence are prevented by nucleation processes that drive the liquid to its crystalline phase.[53]

Water anomalies[61,62] and indications of water polymorphism in ionic aqueous solutions have been experimentally detected.[63–66] Recently in molecular dynamics studies[38,39,67] of supercooled NaCl (aq) it has been shown that in the presence of ions at moderate concentration, the LDL–HDL coexistence is still detectable but ions can shift the phase diagram of supercooled water, opening the possibility that the liquid–liquid transition could be explored by experiments on ionic solutions. This result is supported by different computer simulations where it was shown that the LLCP of water-like models in hydrophobic solutes exists and is shifted in the thermodynamic plane with respect to the predictions in the absence of solutes.[68,69]

An important aspect is the role of the ionic concentration. Computer simulation found that at increasing salt concentration in NaCl (aq) the region of existence of the LDL phase is reduced since ions are more easily solvated in the HDL phase.[67]

From this point of view it is important to understand how different ionic solutes can affect the properties of supercooled water as a function of concentration.

In this paper we consider the structural properties of aqueous solutions of NaCl and KCl salts. According to the Hofmeister classification, Na and K ions would behave respectively as structure makers and structure breakers. We will compare the properties of the two systems at the same thermodynamic conditions. The simulations are performed at ambient pressure, at the same increasing concentration for the two solutions. We explore in particular the changes of the structure upon supercooling.

In this way we can determine how the thermodynamic conditions and the concentration could change the effects of the ions on water going from ambient to supercooled temperature.

We also present results on KF (aq) solutions to study the effects of changing Cl with a cation with a larger charge density which is considered a structure maker in the Hofmeister scale.

The paper is structured as follows. In Section 2 we explain the model employed and the details of the simulations performed. In Section 3 we present the results for the water–water structure in NaCl (aq) and KCl (aq) solutions. In Section 4, we report the ion–water structure for these solutions and we show the structural results of KF (aq). In Section 5 we draw the conclusions.

2 Models and methods of simulation

Computer simulations were carried out with the Molecular Dynamics (MD) method. Water is described by the TIP4P site model where the molecule is represented by a four

site rigid system. Hydrogens (H) are represented by two positively charged sites connected to the neutral oxygen (O) site, whose negative charge is shifted and attributed to the fourth site (X). The OH bond length is 0.9572 Å, the angle between the two bonds is $\theta = 104.5°$. The X site lies in the molecular plane shifted 0.15 Å from the oxygen, the OX bond forms an angle $\theta/2$ with the OH bonds. To each H site is attributed a charge of $0.52e$, these positive charges are neutralized by the negative X charge. The interactions between the sites of the water molecule, the ions and water sites with ions were modeled with the combination of the coulombic and the Lennard-Jones (LJ) potential

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

The Jensen and Jorgensen interaction parameters[70] were assumed for the LJ interaction of the ions. The ion–ion and the ion–water LJ parameters were calculated by using the geometrical mixing rules $\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{1/2}$ and $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha}\sigma_{\beta\beta})^{1/2}$

All the LJ parameters are reported in Table 1. These parameters reproduce very well the structural characteristics and free energies of hydration of the ions.

The simulations were performed with $N_w + N_{ions} = 512$ and the same number $N_{ions}/2$ of anions and cations, for the different concentrations: $N_w = 500$ for $c = 0.67$ mol kg^{-1}, $N_w = 488$ for $c = 1.36$ mol kg^{-1}, $N_w = 476$ for $c = 2.10$ mol kg^{-1}, $N_w = 448$ for $c = 3.96$ mol kg^{-1}.

Periodic boundary conditions were applied. The interaction potentials were truncated at $r_{cut} = 10$ Å. The long range electrostatic interactions were taken into account with the Ewald particle mesh method. The integration time step was fixed at 1 fs.

The simulations were performed at constant pressure and temperature with the use of the Berendsen thermostat and barostat. The pressure was fixed at ambient conditions, 1.01325 bar, for all the simulations. The equilibration time was 20 ns and the averages were calculated on production runs of 30 ns.

The parallelized version of the GROMACS package has been used.

Table 1 Lennard-Jones parameters of the interactions between oxygen atoms in the TIP4P water molecule, between ions and between ions and oxygen. H and X sites of water interact only by the Coulomb potential

	ε (kJ mol^{-1})	σ (Å)
OO	0.649	3.154
NaNa	0.002	4.070
NaCl	0.079	4.045
KK	0.002	5.170
KCl	0.079	4.559
ClCl	2.971	4.020
NaO	0.037	3.583
KO	0.037	4.038
ClO	1.388	3.561
FF	2.971	3.050
KF	0.079	3.971
FO	1.388	3.102

3 Water structure

The effect of salt on the structure of water is illustrated in Fig. 1 where we report the radial distribution functions (RDF), $g_{OO}(r)$, for NaCl (aq) at different concentrations and temperatures. For comparison we report also the OO RDF for pure TIP4P water.

The $g_{OO}(r)$ for KCl (aq) is practically identical and it is not reported. While the O–O structure is strongly perturbed when the concentration is increased, there are no relevant changes in the $g_{OH}(r)$ and $g_{HH}(r)$ with concentration and temperature. In Fig. 2 the $g_{OH}(r)$ for the NaCl (aq) is reported as an example, the same trend is found for the KCl (aq).

The $g_{OO}(r)$ at $T = 300$ K is little affected at low concentration, but the structure becomes very different from pure ambient water when the concentration is increased, particularly in the region of the second peak. The effect is a progressive rising of the first minimum with a corresponding penetration of the second to the first shell. At the highest concentration the second shell appears collapsed on the first one with the consequent broadening of the first peak. A shift of the third peak to lower r with increasing concentration can be also observed .

Upon supercooling ($T = 220$ K), there is an evident enhancement of the first and the second peaks. The first shell becomes more rigid to penetration from the second shell.
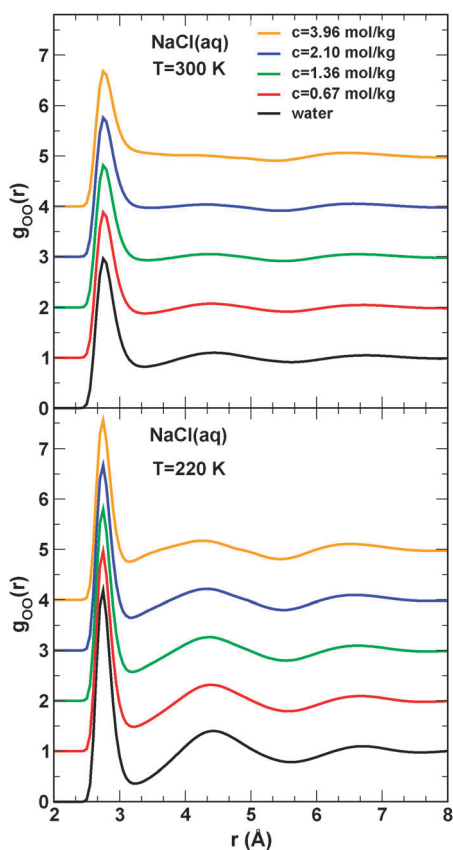

Fig. 1 Oxygen–oxygen RDF of water in NaCl (aq) solution at increasing concentration compared with pure TIP4P water, upper panel $T = 300$ K, bottom panel $T = 220$ K.
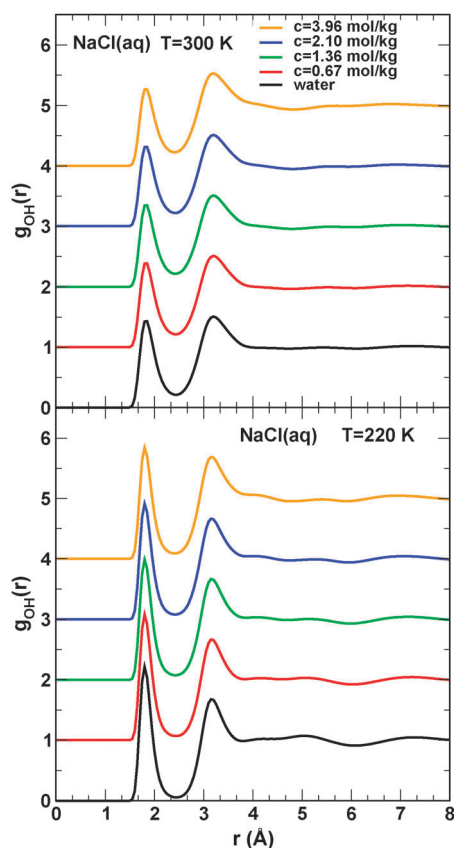

Fig. 2 Oxygen–hydrogen RDF of water in NaCl (aq) solution at increasing concentration compared with pure TIP4P water.

However the modifications of the water structure under the effect of increasing concentration are similar to the ones observed at ambient conditions. The second shell upon increasing concentration becomes broader while the penetration toward the first shell increases. These effects at such a low temperature can be attributed to strong changes in the oxygen–oxygen arrangement. The HB network, although distorted, is however well preserved also at low temperatures as evident from Fig. 2. A similar effect could be obtained by increasing applied pressure on pure water.[16,36]

We observe that the combination of a broadening of the second peak of the $g_{OO}(r)$ and persistence of the HB network characterizes the HDL phase of water.[71] The effect of the ionic concentration both at ambient and supercooled conditions is a progressive transformation of water to an HDL like structure. These results are in agreement with previous simulations on NaCl (aq) where it was found that there is a progressive shrinkage of the LDL region at increasing solute concentration.[39,67] We note moreover that the effect of the presence of salt on water structure does not seem to depend on the particular species of ion involved.

It is interesting also to look at how the ions affect the diffusion of water. In Table 2 we report the diffusion coefficients of oxygens as derived from the GROMACS routine. Apart from some differences between the aqueous solutions, there is a common feature: diffusion is slower than bulk at ambient temperature and upon increasing concentration. At 220 K, diffusion is faster than bulk at a lower salt content

Table 2 Diffusion coefficient of the oxygen at $T = 300$ K and $T = 220$ K for bulk TIP4P water and the aqueous solutions at different concentrations

$D \times 10^{-5}$ (cm^2 s^{-1})				
$T = 300$ K				
c (mol kg^{-1})		NaCl (aq)	KCl (aq)	KF (aq)
Bulk	3.588			
0.67		3.232	3.657	3.053
1.36		2.990	3.239	2.839
2.10		2.471	2.959	2.449
3.96		2.109	2.367	1.656
$T = 220$ K				
c (mol kg^{-1})		NaCl (aq)	KCl (aq)	KF (aq)
Bulk	0.144			
0.67		0.189	0.204	0.165
1.36		0.164	0.207	0.169
2.10		0.167	0.224	0.172
3.96		0.124	0.201	0.093

and decreases upon increasing concentration; this behaviour is compatible to that of bulk water under pressure.[29,72]

4 Hydration shells

4.1 Cation hydration shell

We consider now more in detail for the aqueous solutions investigated how the hydration shell of the cations depends on the concentration and the temperature.

We report in Fig. 3 and 4 the behaviour of the cation–water radial RDF $g_{ZO}(r)$ and $g_{ZH}(r)$ where Z indicates the Na or the K cation. The functions are reported for the NaCl (aq) and KCl (aq) systems at increasing ion concentrations and temperatures $T = 300$ K and $T = 220$ K.

From the figures we observe that the position of the first peak does not change with increasing ion concentration or decreasing temperature for both ZO and ZH RDF.

The height of the first peak increases upon supercooling, as expected, and we observe a slight decrease of the first peak upon increasing concentration only for the NaO RDF.

In Table 3 we report the values of the positions of the first peak ($r_{\alpha\beta}$) of the cation–water and anion–water RDF at the concentration of 0.67 mol kg^{-1} and $T = 300$ K, these values are practically unchanged at the different conditions.

The second column in 3 indicates that in spite of the different cations the positions of the main peak of each ion–water pair is located at the same positions when the distances are rescaled with the repulsive ion–water potential parameter σ_{ZO}. This implies some similarity in the ion–water mean force potential for the different solutions.

The $g_{NaO}(r)$ show a higher first peak intensity than the $g_{KO}(r)$ at all the concentrations and temperatures since the Na ion has a larger charge density. This does not necessarily imply that the K ions have a much weaker interaction with water. As pointed out for instance in ref. 15, another quantity to consider is the number of nearest neighbours, the coordination number (CN). In a fluid system the CN around an atom taken in the origin can be reasonably defined when due to the atomic effective interaction the RDF shows a first peak and then
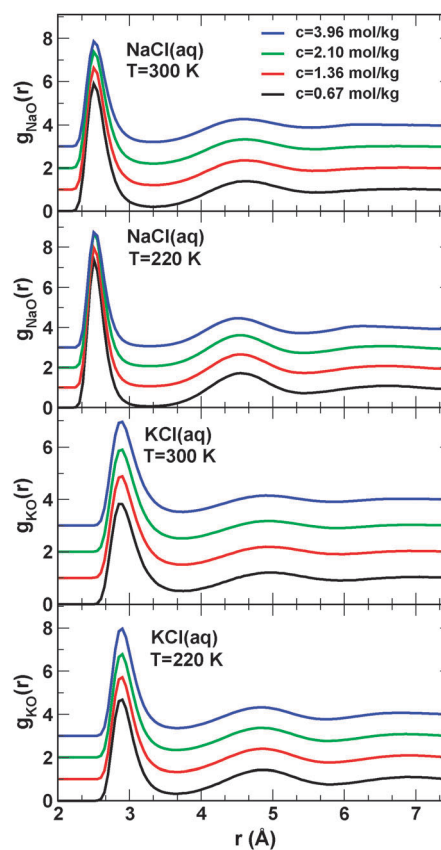

Fig. 3 Cation–oxygen RDF $g_{NaO}(r)$ on the two top panels and $g_{KO}(r)$ on the two bottom panels for increasing concentration and temperatures $T = 300$ K and $T = 220$ K.

decreases toward a minimum before the appearance of a second peak. This happens at liquid density and the CN can be calculated as

$$n_{\alpha\beta}^{(1)} = \frac{N_\beta}{V} \int_0^{r_{\alpha\beta}^{(1)}} 4\pi r^2 g_{\alpha\beta}(r) dr \qquad (2)$$

where $r_{\alpha\beta}^{(1)}$ is the radius of the first $\alpha - \beta$ shell, this radius is usually coincident with the position of the minimum after the peak.

We report the CN for the ZO, ZH first shell in Fig. 5. In spite of small fluctuations due to some uncertainty in the location of $r_{\alpha\beta}^{(1)}$ for the broadening of the first minimum, there are evident trends. In both cases there is a decrease of the CN at increasing concentration. The KO CN are systematically higher than the NaO CN. The integral (2) is in fact determined from the intensity of the peak and the broadening of the area below it weighted with the term r^2. The shift to larger r of the first minimum of $g_{KO}(r)$ is the reason for the higher CN as compared with the that of $g_{NaO}(r)$. This shift is due to the difference in the range of the ZO interaction. These results indicate that the strength of the ion–water interaction cannot simply be deduced by comparing the heights of the ion–water RDF.

Coming back to Fig. 3–4 we observe that upon concentration of ions the second and third shell of the $g_{ZO}(r)$ and $g_{ZH}(r)$ move to lower distances. This effect is small for KCl
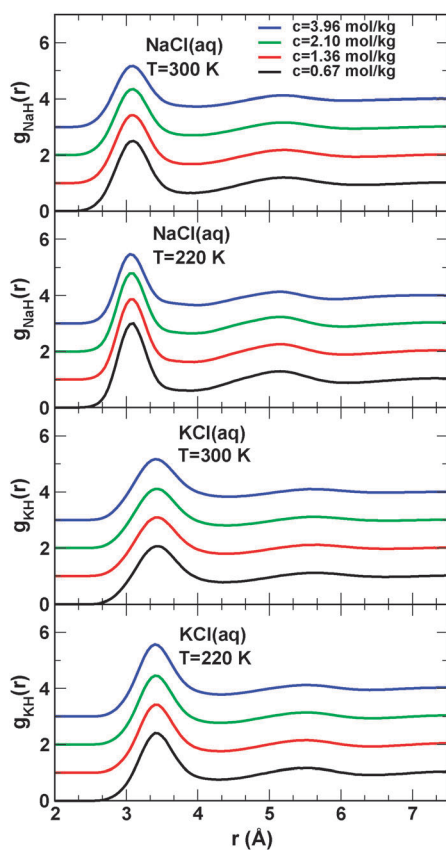
Fig. 4 Cation–hydrogen RDF $g_{NaH}(r)$ on the two top panels and $g_{KH}(r)$ on the two bottom panels for increasing concentration and temperatures $T = 300$ K and $T = 220$ K.

Table 3 Positions of the first peak of the different ion–water RDF at $T = 300$ K and $c = 0.67$ mol kg^{-1}. α indicates the ion while β indicates a water O or H site

	$r_{\alpha\beta}$ (Å)	$r_{\alpha\beta}/\sigma_{\alpha O}$
NaO	2.50	0.70
NaH	3.10	0.86
ClO (NaCl)	3.25	0.91
ClH (NaCl)	2.35	0.66
KO	2.90	0.72
KH	3.45	0.85
ClO (KCl)	3.25	0.91
ClH (KCl)	2.35	0.66

(aq) and more marked for NaCl (aq). The largest shift in particular is found for the third shell of NaCl (aq). This shows that the water–ion interaction has effects well beyond the first hydration shell causing a shrinkage of the structure surrounding the ion as concentration is increased similarly to the increase of pressure, as found in experiment.[15]

In Fig. 6 we compare the cation–oxygen and cation–hydrogen RDF for the lower and the higher concentrations. The $g_{ZO}(r)$ are reported with the abscissa rescaled to the r_{ZO} in order to show more in details the differences between the hydration shells of the two cations.

It is evident in all the cases that a well defined shell of oxygen is formed around the cation but there are differences between the hydration shells of KO and NaO. In particular the
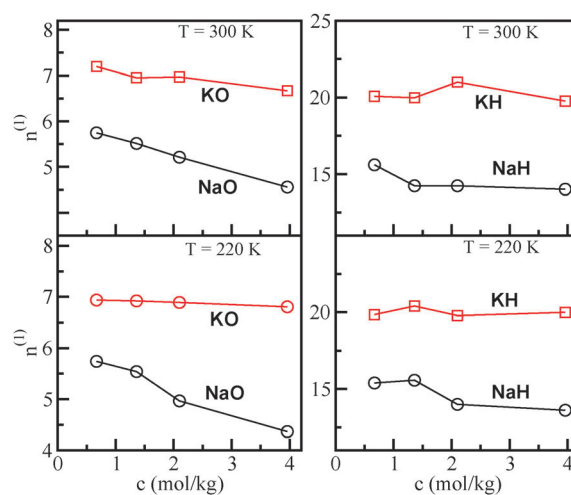

Fig. 5 NaO and KO coordination numbers calculated with eqn (2) as function of concentration for both the aqueous solutions at the different temperatures as indicated in the panels of the figure.
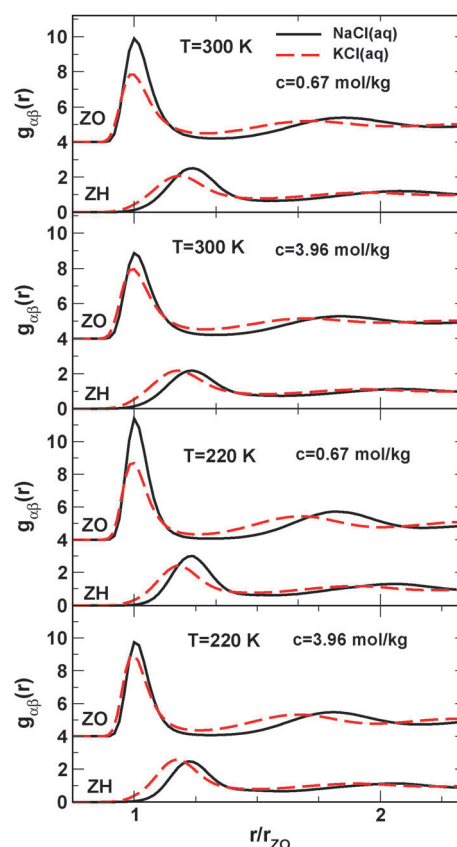

Fig. 6 ZO and ZH RDF for NaCl (aq) (bold line) and KCl (aq) (dashed line) reported as a function of the respective r/r_{ZO}. The two concentrations $c = 0.67$ mol kg^{-1} and $c = 3.96$ mol kg^{-1} are reported for the temperatures $T = 300$ K and $T = 220$ K as indicated in the panels.

first KO shell is less rigid since the peak appears lower and the minimum is broader. The KO second hydration shell is closer to the first one as compared with the corresponding shells of the NaCl (aq) solution. In agreement with experimental findings[15] these results can be interpreted as an evidence of a

decreased orientational order of water molecules in the K hydration shell with respect to the hydration shell around Na ions. We note moreover that in the KCl (aq) solution there is the possibility of exchanging molecules between the first and the second shell as found in experiments,[15] previous computer simulation[17] and *ab initio* calculations.[73] This property is preserved even upon supercooling. On the contrary the first shell of the NaO becomes more rigid at $T = 220$ K.

The increase in concentration has more effect on the NaCl (aq) hydration shell. This is evident also from the slope of the NaO CN *vs.* c in comparison with the corresponding KO CN, see Fig. 5. At low concentration upon supercooling, the hydration shell of Na tends to stabilize and to become more rigid. At the highest concentration we note the decrease of the $g_{NaO}(r)$ peak as function of T. This can be due to differences in the thermodynamic behaviour between the two solutions in approaching the HDL phase of the solvent with a tendency to demixing of the NaCl (aq).

Looking at the $g_{ZH}(r)$ it is evident that the Z cations, due to the positive charge, shifts the hydration shell of hydrogens to larger distances with respect to the ZO and the distribution of hydrogens around the Z cations appears broader.

4.2 Chloride hydration shell

At variance with the ZO structure, the $g_{ClO}(r)$ and $g_{ClH}(r)$ reported in Fig. 7 and Fig. 8 show a different behaviour for NaCl (aq) and for KCl (aq).
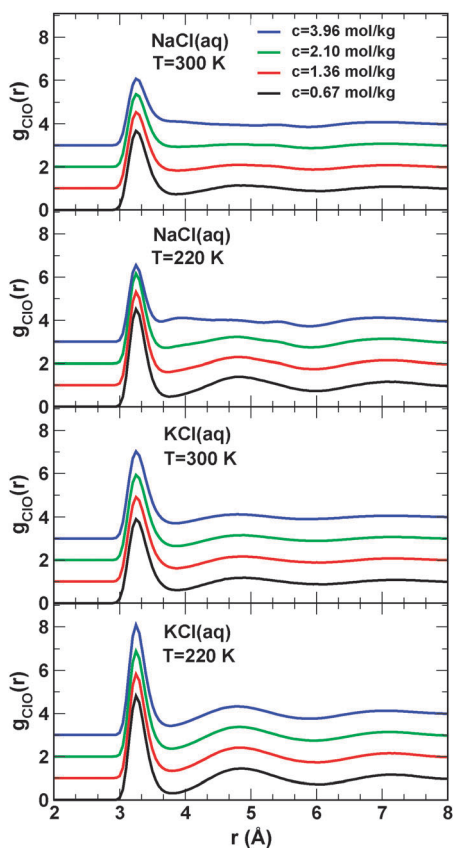

Fig. 7 Chloride–oxygen $g_{ClO}(r)$ RDF for NaCl (aq) on the two top panels and KCl (aq) on the two bottom panels for increasing concentration and temperatures $T = 300$ K and $T = 220$ K.
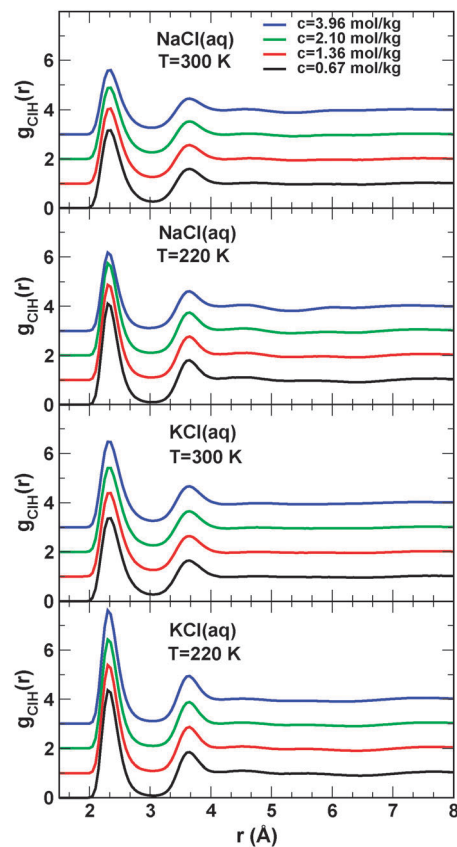

Fig. 8 Chloride–hydrogen g_{ClH} RDF for NaCl (aq) on the two top panels and KCl (aq) on the two bottom panels for increasing concentration and temperatures $T = 300$ K and $T = 220$ K.

The increase in salt concentration has little effect on the ClO RDF in KCl (aq) while a strong change is observed in the region of the second peak for NaCl (aq).

The $g_{ClH}(r)$ show well defined first and second peaks. For NaCl (aq), at increasing concentration there is a decrease of the first peak in correspondence with the progressive disappearing of the second hydration shell in the ClO. In KCl (aq) the first hydrogen shell is almost independent from the concentration.

The changes with concentration are reflected also in the CN for the ClO, ClH (not reported). There is not much change in CN in KCl (aq) while in NaCl (aq) it is possible to note a decrease of CN as function of c, particularly evident for the ClH CN.

The behaviour of the chloride hydration shell can be observed in Fig. 9, where the $g_{ClO}(r)$ and $g_{ClH}(r)$ are reported. The coordination shells of both oxygens and hydrogens are well defined for all the concentrations and temperatures.

It is evident that at low concentration both at $T = 300$ K and $T = 220$ K, the hydration shell of chloride ions does not depend on the cation. This is confirmed from the behaviour of the Cl–O CN.

As evidenced from the sharp first ClH peak at all concentrations and temperatures for both the solutions, chloride ions can form linear hydrogen bonds with hydrogen atoms. The distance between the first peak of g_{ClH} and g_{ClO} is approximately 1 Å, this indicates the tendency of the hydrogens to form almost linear bridges between oxygens and chlorine.[15]
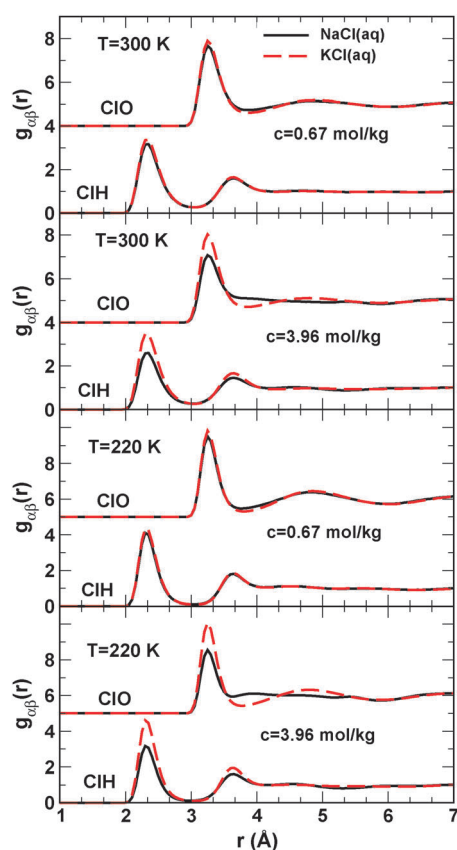
Fig. 9 ClO and ClH RDF for NaCl (aq) and KCl (aq). The two concentrations $c = 0.67$ mol kg^{-1} and $c = 3.96$ mol kg^{-1} are reported for the temperatures $T = 300$ K and $T = 220$ K as indicated in the panels.

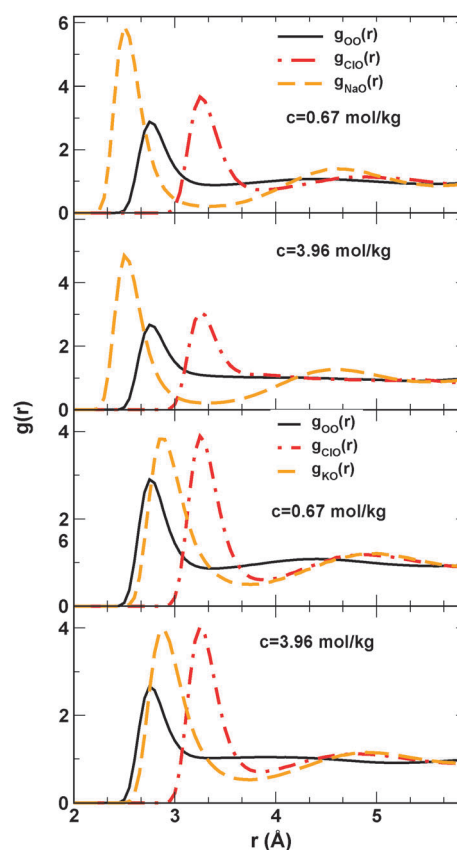**Fig. 10** OO, ClO and ZO RDF at $T = 300$ K for NaCl (aq) on the top panels and KCl (aq) on the bottom panels. Concentrations are $c = 0.67$ mol kg^{-1} and $c = 3.96$ mol kg^{-1}, as indicated.

From the same Fig. 9, it is also evident that as the concentration increases the behaviour of NaCl (aq) starts to be different from that of the KCl (aq). At low concentration the $g_{ClO}(r)$ is similar in both the solutions. While, at the highest concentration in KCl (aq), the ClO–ClH RDF do not change much with respect to the lowest concentration we observe that in the NaCl (aq) system there is a decrease of the first peak both in the $g_{ClO}(r)$ and $g_{ClH}(r)$. In particular the second hydration shell of O around Cl ions disappears at $T = 300$ K and it becomes a small shoulder at $T = 220$ K. These results are in contradiction with the hypothesis of an independence of the hydration shell of chloride from concentration.[8] From our results, in fact, it comes out that the behaviour of the hydration shell is related to the thermodynamic conditions.

As shown above in the analysis of the water–water structure the systems, upon increasing salt concentration, undergo a transformation to the HDL phase of the solvent.

By comparing the $g_{ClO}(r)$ and g_{ClH} in Fig. 7 and 8 with the $g_{OO}(r)$ and $g_{OH}(r)$ RDF in Fig. 1 and 2 it appears that in NaCl (aq), the structure of the chlorine hydration shells is similar to the structure of the OO and OH shells for both the temperatures. Cl can be approximately substitutional to O for both temperatures and all concentrations. In KCl (aq), instead the $g_{KO}(r)$, shown in Fig. 9 does not follow the changes taking place in the $g_{OO}(r)$ at increasing concentration (Fig. 1).

In Fig. 10 we show the functions $g_{OO}(r)$ and $g_{ClO}(r)$ together with the $g_{ZO}(r)$ for the salt solutions at different concentration.

In NaCl (aq) the NaO is on the left side of the OO peak, while in KCl (aq) the KO peak is shifted to higher r and becomes intermediate between the peaks of OO and ClO. In KCl (aq) the positive K ions are closer to the O and they have a larger diameter than the Na ions. At increasing concentration it appears that steric effects of K ions on oxygens keep rigid the first ClO shell preventing a full rearrangement of the chlorine hydration shell. In calculations on electrolyte solutions it was found that excluded volume effects are stronger between ions and a sphere with opposite charge.[74]

In spite of this, the effect of K and Na cations on the water structure are very similar.

4.3 Results for KF (aq) solutions

As a further example to test the previous results we consider the KF (aq) solutions, where the *structure breaker* Cl anions are substituted with the F anions, which has a larger charge density and is considered as a *structure maker*.

In the KF (aq) solutions the $g_{KO}(r)$ and $g_{KH}(r)$ are very similar to the functions shown in Fig. 3 and they are not reported. It comes out that the KO structure is independent on the anion.

It is more interesting to observe the $g_{FO}(r)$ and $g_{FH}(r)$ in Fig. 11. By comparing with the corresponding chlorine–water RDF in Fig. 7 and 8, a more well defined hydration structure is evident here due to the higher charge density of F ions. This would seem in agreement with the classification of F as a structure maker with respect to Cl. However from the RDF of
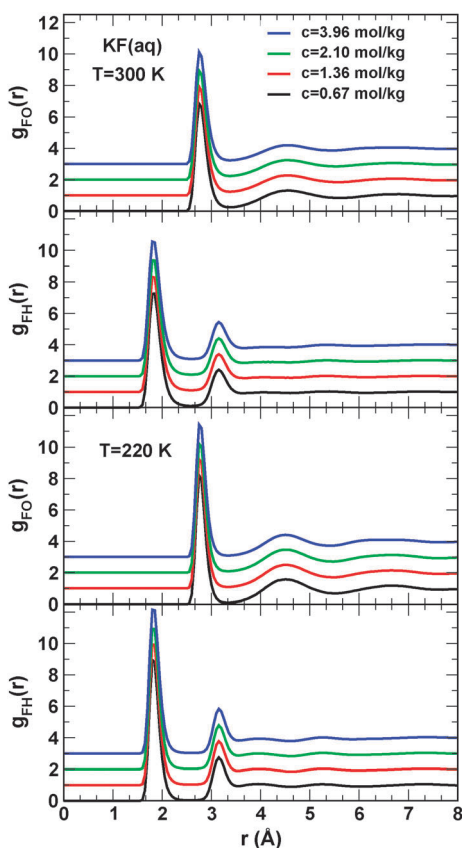
Fig. 11 FO and FH RDF for KF (aq) for increasing concentration and temperatures $T = 300$ K and $T = 220$ K, as indicated in the panels.

Fig. 12 Oxygen–oxygen RDF of water in the KF (aq) solution at increasing concentration compared with pure TIP4P water, upper panel $T = 300$ K, bottom panel $T = 220$ K.

water in KF (aq) in Fig. 12 it is evident that the water structure undergoes the same changes observed in the other aqueous solutions, with a progressive approach of water to its HDL structure.

As before for the KCl (aq) we find that the position of the first KO peak is on the high r side of the FO peak position. It comes out that also the structure of the hydration shells of KF (aq) appears to be determined from the interplay between the charge density and the steric effects.

5 Conclusions

In this work we have investigated by means of computer simulations two salt water mixtures, NaCl (aq) and KCl (aq). The salts are formed by the same anion, considered a structure breaker in the traditional classification, and a cation considered a structure maker, the Na, and a cation considered a structure breaker, the K. We performed the simulations at different ionic concentrations and we compared the results at ambient temperature and upon supercooling at $T = 220$ K at ambient pressure value.

In agreement with recent experimental results we find that the concept of structure maker/breaker does not seem to appropriately take into account the effects of ions on the water structure. It is in fact true that for the cation hydration shells the arrangement of water around the K ions has a weaker order with respect to water molecules in the hydration
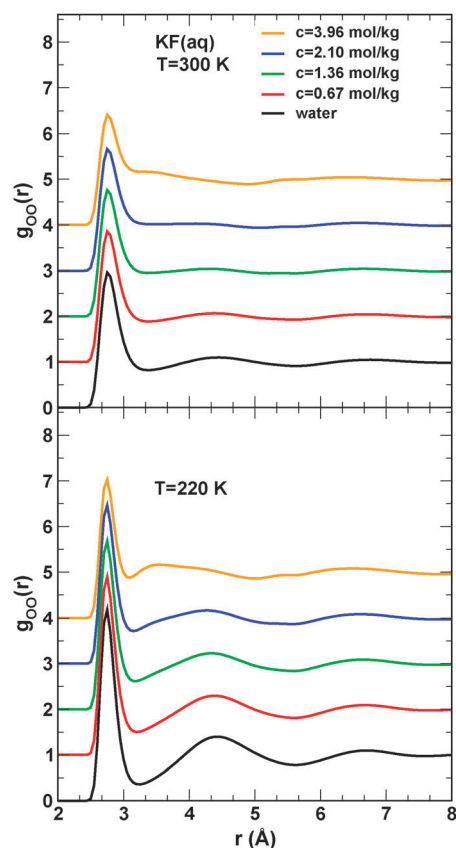
shells of Na ions, but when we look to the water structure, we find a strong distortion of the HB network upon increasing the concentration in both NaCl (aq) and KCl (aq) with not many differences between the two cases.

We observe in particular, in agreement with previous results on NaCl (aq),[38,39,67] a tendency of water to transform to the HDL phase upon increasing ion concentration.

From our calculations, the structure of water appears weakly dependent on the type of salt. It seems that as the ions are hydrated, the structure of water, for the given thermodynamic conditions, is only affected by the level of concentration. Our results on the effects of the perturbation of the HB network both in NaCl (aq) and KCl (aq) support the hypothesis of an analogy between concentration of ions in solution and enhancement of external pressure applied to pure water.

The results on KF (aq) are in agreement with these considerations.

The behaviour of the cation–oxygen and anion–oxygen structures with concentration indicates that charge density and steric effects are relevant in the formation of more or less rigid hydration shells, but they scarcely influence the water structure.

An important finding of this paper is that the concept of structure makers and structure breakers cannot prescind from the other ionic species present in the solution. In fact differences between the behaviour of the hydration shell of Cl in NaCl

(aq) in and KCl (aq) are found. They can be explained in terms of the different charge density and size of the cations involved.

From our study it is confirmed that the structure making/breaking classification of ions is not able to give a complete prediction of the way in which water structure changes under the effect of ions. This appears more evident upon supercooling.

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References

1 A. K. Covington andT. H. Lilley,*Ionic Processes in Solutions*, Dover, New York,1953.
2 A. K. Covington and T. H. Lilley, *Electrochemistry*, The Chemical Society, London, 1970, vol. 1, p. 1.
3 F. Hofmeister, *Naunyn-Schmiedebergs Arch. Pharmacol.*, 1888, **24**, 247.
4 K. D. Collins, *Methods*, 2004, **34**, 300.
5 Y. Zhang and P. S. Cremer, *Curr. Opin. Chem. Biol.*, 2006, **10**, 658.
6 J. H. Morais-Cabral, Y. Zhouh and R. MacKinnon, *Nature*, 2001, **414**, 37.
7 G. W. Neilson and J. E. Enderby, *Proc. R. Soc. London, Ser. A*, 1983, **390**, 353.
8 J. E. Enderby, *Chem. Soc. Rev.*, 1995, **24**, 159.
9 G. W. Neilson and G. J. Herdman, *J. Mol. Liq.*, 1990, **46**, 165.
10 H. Ohtaki and T. Radnai, *Chem. Rev.*, 1993, **93**, 1147.
11 H. Ohtaki, *Monatsh. Chem.*, 2001, **132**, 1237.
12 A. K. Soper, *J. Chem. Phys.*, 1994, **101**, 6888.
13 G. W. Neilson, P. E. Mason, S. Ramos and D. Sullivan, *Philos. Trans. R. Soc. London, Ser. A*, 2001, **359**, 1575.
14 Y. J. Lü and B. Wei, *J. Chem. Phys.*, 2006, **125**, 144503.
15 R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci and A. K. Soper, *J. Phys. Chem. B*, 2007, **111**, 13570.
16 R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci and A. K. Soper, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2959.
17 R. W. Impey, P. A. Madden and I. R. McDonald, *J. Phys. Chem.*, 1983, **87**, 5071.
18 S. B. Zhu and G. W. Robinson, *J. Chem. Phys.*, 1992, **97**, 4336.
19 R. M. Lynden-Bell, J. C. Rasaiah and J. P. Noworyta, *Pure Appl. Chem.*, 2001, **73**, 1721.
20 S. Koneshan, J. C. Rasaiah, R. M. Lynden-Bell and S. H. Lee, *J. Phys. Chem. B*, 1998, **102**, 4193.
21 S. Koneshan and J. C. Rasaiah, *J. Chem. Phys.*, 2000, **113**, 8125.
22 J. C. Rasaiah and R. M. Lynden-Bell, *Philos. Trans. R. Soc. London, Ser. A*, 2001, **359**, 1545.
23 A. Chandra, *Phys. Rev. Lett.*, 2000, **85**, 768.
24 S. Chowdhuri and A. Chandra, *J. Chem. Phys.*, 2001, **115**, 3732.
25 S. Chowdhuri and A. Chandra, *J. Chem. Phys.*, 2003, **118**, 9719.
26 L. Degrève and F. L. B. D. Silva, *J. Mol. Liq.*, 2000, **87**, 217.
27 D. S. Vieira and L. Degrève, *J. Mol. Struct.*, 2002, **580**, 127.
28 M. Patra and M. J. Karttunen, *J. Comput. Chem.*, 2004, **25**, 678.
29 J. S. Kim and A. Yethiraj, *J. Phys. Chem. B*, 2008, **112**, 1729.
30 H. Du, J. C. Rasaiah and J. D. Miller, *J. Phys. Chem. B*, 2007, **111**, 209.
31 I. S. Joung and T. E. Cheatham-III, *J. Phys. Chem. B*, 2008, **112**, 9020.
32 P. Auffinger, T. E. Cheatham-III and A. C. Vaiana, *J. Chem. Theory Comput.*, 2007, **3**, 1851.
33 J. Alejandre and J. P. Hansen, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 061505.
34 P. J. Lenart, A. Jusufi and A. Z. Panagiatopoulos, *J. Chem. Phys.*, 2007, **126**, 044509.
35 C. J. Fennell, A. Bizjak, V. Vlachy and K. A. Dill, *J. Phys. Chem. B*, 2009, **113**, 6782.
36 J. Holzmann, R. Ludwig, A. Geiger and D. Paschek, *Angew. Chem., Int. Ed.*, 2007, **46**, 8907.
37 D. Corradini, P. Gallo and M. Rovere, *J. Chem. Phys.*, 2008, **128**, 244508.
38 D. Corradini, M. Rovere and P. Gallo, *J. Chem. Phys.*, 2010, **132**, 134508.
39 D. Corradini, M. Rovere and P. Gallo, *J. Phys. Chem. B*, 2011, **115**, 1461.
40 V. A. Parsegian, *Nature*, 1995, **378**, 335.
41 D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.
42 W. M. Cox and J. H. Wolfenden, *Proc. R. Soc. London, Ser. A*, 1934, **145**, 486.
43 B. Hribar, N. T. Southall, V. Vlachy and K. A. Dill, *J. Am. Chem. Soc.*, 2002, **124**, 12302.
44 A. K. Soper and K. Weckström, *Biophys. Chem.*, 2006, **124**, 180.
45 R. Leberman and A. K. Soper, *Nature*, 1995, **378**, 364.
46 P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Nature*, 1992, **360**, 324.
47 P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1993, **48**, 3799.
48 O. Mishima, L. D. Calvert and E. Whalley, *Nature*, 1985, **76**, 314.
49 R. Martonak, D. Donadio and M. Parrinello, *J. Chem. Phys.*, 2005, **122**, 134501.
50 K. Winkel, M. Elsaesser, E. Mayer and T. Loerting, *J. Chem. Phys.*, 2008, **128**, 044510.
51 C. U. Kim, B. Barstow, M. V. Tate and S. M. Gruner, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 4596.
52 P. G. Debenedetti and H. E. Stanley, *Phys. Today*, 2003, **56**, 40.
53 P. G. Debenedetti, *J. Phys.: Condens. Matter*, 2003, **15**, R1669.
54 H. Poole, I. Saika-Voivod and F. Sciortino, *J. Phys.: Condens. Matter*, 2005, **17**, L431.
55 M. Yamada, S. Mossa, H. Stanley and F. Sciortino, *Phys. Rev. Lett.*, 2002, **88**, 195701.
56 P. Jedlovszky and R. Vallauri, *J. Chem. Phys.*, 2005, **122**, 081101.
57 I. Brovchenko, A. Geiger and A. Oleinikova, *J. Chem. Phys.*, 2005, **123**, 044515.
58 Y. Liu, A. Z. Panagiotopoulos and P. G. Debenedetti, *J. Chem. Phys.*, 2009, **131**, 104508.
59 J. L. F. Abascal and C. Vega, *J. Chem. Phys.*, 2010, **133**, 234502.
60 J. L. F. Abascal and C. Vega, *J. Chem. Phys.*, 2011, **134**, 186101.
61 D. G. Archer and R. W. Carter, *J. Phys. Chem. B*, 2000, **104**, 8563.
62 R. W. Carter and D. G. Archer, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5138.
63 O. Mishima, *J. Chem. Phys.*, 2005, **123**, 154506.
64 O. Mishima, *J. Chem. Phys.*, 2007, **126**, 244507.
65 L. E. Bove, S. Klotz, J. Philippe and A. M. Saitta, *Phys. Rev. Lett.*, 2011, **106**, 125701.
66 K. Winkel, M. Seidl, T. Loerting, L. E. Bove, S. Imberti, V. Molinero, F. Bruni, R. Mancinelli and M. A. Ricci, *J. Chem. Phys.*, 2011, **134**, 024515.
67 D. Corradini and P. Gallo, *J. Phys. Chem. B*, 2011, in press, DOI: 10.1021/jp2045977.
68 S. Chatterjee and P. G. Debenedetti, *J. Chem. Phys.*, 2006, **124**, 154503.
69 D. Corradini, S. V. Buldyrev, P. Gallo and H. E. Stanley, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2010, **81**, 061504.
70 K. P. Jensen and W. L. Jorgensen, *J. Chem. Theory Comput.*, 2006, **2**, 1499.
71 A. K. Soper and M. A. Ricci, *Phys. Rev. Lett.*, 2000, **84**, 2881.
72 F. W. Starr, S. Harrington, F. Sciortino and H. E. Stanley, *Phys. Rev. Lett.*, 1999, **82**, 3629.
73 L. M. Ramaniah, M. Bernasconi and M. Parrinello, *J. Chem. Phys.*, 1999, **111**, 1587.
74 P. Strating and F. W. Wiegel, *J. Phys. A: Math. Gen.*, 1993, **26**, 3383.