Thermodynamics of supercooled water in solutions

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Abstract. Molecular dynamics simulations are performed on bulk TIP4P water and on a low concentration aqueous sodium chloride solution. The thermodynamic properties of the systems are studied by analysing the isotherms and the isochores planes. The comparison of the thermodynamics planes of the two systems reveals that modifications beyond a trivial shift occur in the solution. Moreover the limit of mechanical stability and the temperatures of maximum density line can be calculated from the analysis of the thermodynamic planes. While the limit of mechanical stability results unaffected by the presence of the ions, the temperatures of maximum density line is both mildly shifted in temperature and modified in shape in the solution, with respect to bulk water. Signatures of the presence of liquid-liquid coexistence are found in the aqueous solution. The results are also compared to water in a hydrophobic environment and to water confined between hydrophobic plates.

1. Introduction and simulation details
Water presents several anomalous thermodynamic behaviours. Some of the most important are the presence of a line of temperatures of maximum density (TMD) in the thermodynamic plane and the divergences of thermodynamic response functions upon supercooling [1, 2].

The existence of a second critical point in the deep supercooled region of water, as the end point of the coexistence line between a low density liquid (LDL) and a high density liquid (HDL) has been hypothesized and its presence has been also observed in several molecular dynamics (MD) simulations [3–8]. In this framework, water thermodynamic anomalies are a consequence of long-range fluctuations induced by the second critical point. Although the deep supercooled region has been so far not directly accessible to experiments, signatures of the presence of a second critical point have been found also experimentally [9].

The properties of water as a solvent are also quite extraordinary [10]. In particular, aqueous solutions of electrolytes are interesting for their role in most biological and geophysical systems. Their thermodynamic properties upon supercooling are not well known so far and an improved understanding would be significant in several fields like for example in cryopreservation of biological tissues [11, 12].

Several important thermodynamics properties such as the melting point, the boiling point and viscosity are known to be affected by the presence of ions. It is therefore interesting to study whether and to what extent the presence of ions affects thermodynamic properties of water upon supercooling. Archer and Carter [13] have shown experimentally that for low NaCl content, up to concentrations

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between 1 and 2 mol/kg at ambient pressure, the TMD and the anomalous behaviour of the isobaric specific heat are still present, while they disappear upon increasing salt concentration.

In this paper we present a MD study of TIP4P bulk water and of a sodium chloride solution in TIP4P water, denoted in the following NaCl(aq), with concentration $c = 0.67$ mol/kg [14]. Both systems are studied upon supercooling. We focus on the isotherms and the isochores planes of the two systems. The analysis of such planes allows the determination of the limit of mechanical stability (LMS) of the liquid with respect to the gas and of the TMD lines.

In our systems the particles interact via a potential given by the sum of a long-range coulombic potential and a short-range Lennard-Jones (LJ) potential. Therefore the interaction potential can be written as

$$U_{ij}(r) = \frac{q_i q_j}{r} + 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^6 - \left(\frac{\sigma_{ij}}{r}\right)^{12}$$

(1)

where $q$ are the electric charges, water-water LJ parameters are those of TIP4P model [15] and ion-ion and ion-water LJ parameters are taken from a reparametrization for LJ potential [16] of Pettitt and Rossky parameters [17] for the Huggins-Mayer potential. The long-range electrostatic interactions are treated by the Ewald summation method and the cutoff radius is set at 9.0 Å.

The MD simulations are performed in the $NVT$ ensemble, employing Berendsen thermostat [18]. The integration timestep used is 1 fs. The simulation box contains 256 water molecules in the case of bulk water, while for the NaCl(aq) it contains 250 water molecules, 3 Na$^+$ ions and 3 Cl$^-$ ions. We simulated densities in the range $0.80$ g/cm$^3 \leq \rho \leq 1.05$ g/cm$^3$ for bulk water and in the range $0.80$ g/cm$^3 \leq \rho \leq 1.1$ g/cm$^3$ for the NaCl(aq). For both systems the range of temperature spanned is $210$ K $\leq T \leq 500$ K. The simulation procedure requires equilibration and production runs and the longest equilibration runs lasted up to 10 ns. We employed the DL_POLY simulation package [19]. Some of the state points for bulk water are taken from a previous work of our group [20].

2. Thermodynamic Results

The thermodynamic properties are studied comparing the isotherms and the isochores planes of bulk water and of NaCl(aq). In particular the TMD and the LMS lines of the two systems are also determined and compared. The LMS can be calculated from the divergence of the isothermal compressibility. The locus of the points for which

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0$$

(2)

is the LMS line. Thus the line joining the minima of the isotherms defines the LMS line. In figure 1 and figure 2 the isotherms of bulk water and NaCl(aq) are shown respectively. Bulk isotherms in the $P$--$\rho$ plane, figure 1, are reported for temperatures ranging from $T = 210$ K to $T = 300$ K. The $T = 300$ K isotherm is the first one showing a minimum, in correspondence of the density $\rho = 0.83$ g/cm$^3$. This minimum remains in correspondence to $\rho = 0.83$ g/cm$^3$ up to the $T = 260$ K isotherms and then shifts to $\rho = 0.85$ g/cm$^3$ for the lower temperatures isotherms. Also for the NaCl(aq) isotherms, figure 2, the first isotherm displaying a minimum is the $T = 300$ K, now in correspondence to $\rho = 0.85$ g/cm$^3$. For all lower temperatures isotherms the minimum is in correspondence to $\rho = 0.87$ g/cm$^3$.

Comparing the two isotherms planes we notice that the NaCl(aq) isotherms minima are shifted to higher densities, with respect to bulk water, and furthermore the envelope of the isotherm lines is globally shifted to lower pressures for the solution. For both systems we can observe that the $T = 220$ K and the $T = 210$ K isotherms present inflections crossing higher temperatures isotherms. This
behaviour has been previously observed in bulk water [3, 21] and it has been interpreted as a signature of the approach of the system to the coexistence between LDL and HDL phases and eventually of the presence of a liquid-liquid (LL) critical point. Therefore it is possible to infer a LL phase coexistence and the existence of a second critical point also in our aqueous solution. As the inflections of NaCl(aq) isotherms are shifted to higher densities with respect to the bulk, we can hypothesize that also the critical point would be shifted to higher densities.

Figure 1. Isotherms of bulk water in the P−ρ plane and LMS line (thick line).

Figure 2. Isotherms of NaCl(aq) solution in the P−ρ plane and LMS line (thick line).
The isochores of bulk water and NaCl(aq) are shown in figure 3 and figure 4 respectively. For both systems the isochores lying below the limit of mechanical stability are not reported. The TMD line can be extracted from the analysis of the isochores plane. The TMD line is the locus of the points where the coefficient of thermal expansion

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

(3)

goes to zero. As the the thermal pressure coefficient is given by

$$\gamma_V = \left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha_p}{K_T}$$

(4)

where $K_T$ is the isothermal compressibility, the TMD line is then defined by the line that joins the minima of the isochores. Polynomial fits of the isochores were performed in order to determine more accurately the minima of the isochores (TMD points).

For bulk water, figure 3, only the four highest densities isochores exhibit a minimum, in the range of temperature explored. The shape of the TMD line for bulk water is in agreement with previous works [6, 21]. In the P–T plane of bulk water the LMS line is also reported and it almost coincides with the $\rho = 0.85$ g/cm$^3$ isochore. The LMS extends to the region of negative pressures and is nonre-entrant down to $T = 210$ K. The behaviour of the LMS line is analogous to what is found in the literature for several water models [4, 6, 21–26].

In figure 4 the isochores of the NaCl(aq) are shown along with the TMD and LMS lines. The isochores of the NaCl(aq) show minima down to the $\rho = 0.90$ g/cm$^3$ isochore. The presence of a TMD in a sodium chloride solution with the concentration studied is in agreement with the experimental work by Archer and Carter [13]. The LMS line for NaCl(aq) practically overlaps with the $\rho = 0.87$ g/cm$^3$ isochore.

**Figure 3.** Isochores of bulk water in the P–T plane, TMD line LMS lines.
The comparison of the isochores planes of the two systems shows that the isochores of the aqueous solution lie at lower pressures with respect to bulk water and that the concavity of the curves close to the minima is markedly deeper in bulk water than in the solution. In figure 5 we report in the P–T plane, the LMS and the TMD lines of bulk water and of NaCl(aq). In the same picture we also show the LMS and TMD lines of TIP4P water confined in a hydrophobic environment, an off-lattice matrix of soft spheres [20]. Always in figure 5 the TMD lines of bulk TIP5P water [23] and of TIP5P water confined between hydrophobic plates [27] are reported.

Let us focus first on the effect of the ions on bulk water. We can notice that the presence of ions induces on the TMD line a mild shift in temperature and a marked modification in shape. Indeed, while the TMD lines of bulk water and of NaCl(aq) span the same range of densities, the range of pressures spanned by the NaCl(aq) TMD is much wider. The modification of the shape of the TMD together with shape modifications in the isotherms and isochores of the NaCl(aq), with respect to the bulk, indicate that the effect of the ions is not limited to give a trivial pressure shift in the phase diagram.

On the other hand, the presence of ions does not seem to affect the position and the shape of the LMS line that remains unaltered in the solution. We can argue that a possible explanation is connected to the fact that the position of the LMS line is mostly determined by the LDL phase. The ions, being hydrophilic, increase the local density of water, so that water around the ions is mostly HDL-like. The concentration of ions is probably too low to affect LDL properties and thus the LMS line does not change in the solution.

As we can see in figure 5, this is not the case for water confined in a hydrophobic environment [20] for which the LMS line is shifted toward higher pressures and reaches also higher temperatures, arriving at T = 350 K. This system resembles a solution of hydrophobic nonpolar solutes in water. Thus it can be argued that, as water density is depleted around hydrophobic solutes, the situation here is different with respect to the case of ionic (hydrophilic) solutes.

The TMD line of TIP4P water in the hydrophobic mixture is very similar to the one of the NaCl(aq) in shape, nonetheless it is shifted by about 220 MPa in pressure and about 20 K in

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**Figure 4.** Isochores of NaCl(aq) solution in the P–T plane, TMD line LMS lines.
Figure 5. TMD and LMS lines in the P–T plane for bulk water, NaCl(aq), the hydrophobic system studied in [20] and TMD lines of TIP5P bulk water [23] and TIP5P water confined between hydrophobic plates studied in [27].

Figure 5. TMD and LMS lines in the P–T plane for bulk water, NaCl(aq), the hydrophobic system studied in [20] and TMD lines of TIP5P bulk water [23] and TIP5P water confined between hydrophobic plates studied in [27].

temperature. Therefore the presence of either hydrophilic or hydrophobic solutes in water seems to broaden the TMD line in a similar way, apart from the shift in the phase diagram due to the confinement. Moreover, the position of the TMD in confined systems depends on what kind of confinement is applied. In fact, in TIP5P water confined by hydrophobic plates, Kumar et al. [27] found that the TMD line is shifted by about 40 K in temperature but they did not observe any pressure shift, with respect to bulk TIP5P water, see figure 5. For the system with hydrophobic soft spheres instead, the shift in temperature is similar but there are also a shift toward higher pressures by about 220 MPa and a broadening of the TMD line.

3. Conclusions

We performed MD simulations of bulk water and of a \( c = 0.67 \) mol/kg aqueous sodium chloride solution upon supercooling. In both cases the TIP4P model was used to model water molecules. Thermodynamic properties of the two systems were studied comparing the respective isotherms P–\( \rho \) planes and the isochores P–T planes. The presence of ions moves both the isotherms and the isochores toward lower pressures and slightly modifies the shape of the curves, especially in proximity of their minima. The analysis of these planes allowed also the determination of the TMD and the LMS lines. Our results were also compared to water in a hydrophobic environment [20], to TIP5P bulk water and to TIP5P water confined between hydrophobic plates [27].

The LMS line is substantially unaltered by the presence of ions, at the chosen concentration, with respect to bulk water, while it lies at higher pressures, reaching also higher temperatures for water in the hydrophobic environment. For all systems the LMS line extends to the region of negative pressures and it is non-re-entrant down to the lowest temperature examined. The different behaviour of the LMS lines in hydrophilic and hydrophobic systems could be connected by the local variation of the density of water induced by the presence of hydrophilic/hydrophobic solutes.

At variance with the LMS line, the TMD line is affected by the presence of the ions. In fact, it results mildly shifted in temperature and markedly modified in shape, with respect to the bulk, while it...
is both significantly shifted in temperature and affected in shape in the hydrophobic mixture. The TMD line is also deeply affected by the kind of (hydrophobic) confinement. While for water confined between hydrophobic plates only a shift in temperature was found, in water containing hydrophobic soft spheres a broadening of the TMD shape and a significant shift toward higher pressures are also present.

Signatures of the presence of LL coexistence were also found for the NaCl(aq) in the inflections of the low temperatures isotherms at high densities.

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