A route to explain water anomalies from results on an aqueous solution of salt

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In this paper we investigate the possibility to detect the hypothesized liquid-liquid critical point of water in supercooled aqueous solutions of salts. Molecular dynamics computer simulations are conducted on bulk TIP4P water and on an aqueous solution of sodium chloride in TIP4P water, with concentration $c = 0.67$ mol/kg. The liquid-liquid critical point is found both in the bulk and in the solution. Its position in the thermodynamic plane shifts to higher temperature and lower pressure for the solution. Comparison with available experimental data allowed us to produce the phase diagrams of both bulk water and the aqueous solution as measurable in experiments. Given the position of the liquid-liquid critical point in the solution as obtained from our simulations, the experimental determination of the hypothesized liquid-liquid critical point of water in aqueous solutions of salts appears possible. © *2010 American Institute of Physics*. [doi:10.1063/1.3376776]

I. INTRODUCTION

In the past years several theoretical and computer simulation studies have hypothesized possible scenarios to explain the thermodynamic anomalies of water in the supercooled region. The *critical point scenario* ascribes the large increase in thermodynamic response functions to the presence of a liquid-liquid (LL) phase transition in the supercooled region between a low density liquid (LDL) and a high density liquid (HDL).[1,2] In this picture the coexistence line between the two liquids terminates in a LL critical point (LLCP). From the LLCP a line of maxima of correlation length, called the Widom line, is emanated.[3] The lines of extrema of several thermodynamic response functions asymptotically merge on the Widom line upon approaching the critical point from higher temperatures.[4]

The anomalous behavior of water can alternatively be related to a *singularity free scenario*[5] in which the increase in thermodynamic response functions is due to local density fluctuations that do not eventually lead to singularities. Recently another picture was proposed, the *critical point free scenario*.[6] In this case the HDL-LDL transition is interpreted as an order-disorder transition of the first order and no LLCP occurs.

Experimental investigation of the deeply supercooled region of bulk water is hampered by nucleation.[7–9] Indications of the existence of LLCP in supercooled bulk water have been found.[10,11] In particular the LLCP was hypothesized to be located at about $T \simeq 220$ K and $P \simeq 100$ MPa.

The critical point scenario was formulated by Poole *et al.*[1] as a result of computer simulations on water with the ST2 potential. This interpretation was confirmed by other simulations on ST2 water,[2,12,13] until the very recent paper by Liu *et al.*[14] The LLCP was also found in water simulated with other potentials.[2,12,15–20] Lattice models of water have

indicated that upon properly tuning the parameters of the models one can switch from one scenario to the other.[5,21,22]

Simulations on spherically symmetric ramp potential particles, mimicking the properties of water, show the existence of LLCP for proper choices of the parameters.[23,24]

Possible experimental routes for the observation of the supercooled region where the LLCP is supposed to exist are therefore timely.

In the natural environment water is almost ever found as a solvent in mixtures of two or more components and water can be more easily supercooled in solutions.[25] Indications of the possible presence of a LLCP in aqueous solutions have been found experimentally,[26–29] theoretically,[30] and in computer simulations.[31,32] Nonetheless the existence and the position of LLCP in the thermodynamic plane for an aqueous solution has not yet been determined either in experiments or in simulations.

Here we present an extensive molecular dynamics (MD) study of TIP4P bulk water and of $c = 0.67$ mol/kg sodium chloride aqueous solution, NaCl(aq), in TIP4P water. This study aims to locate the position of the LLCP in the aqueous solution and to compare it with the LLCP of bulk water in order to see if a measure of the LLCP is experimentally feasible in the solution. We selected this particular concentration because it was found in experiments that it is high enough to show deviation from the bulk behavior but not so high to destroy water anomalies.[26] The chosen salt concentration is close to that of seawater $c \sim 0.55$ mol/kg and it is well above the physiological concentration which is $c \sim 0.15$ mol/kg.

The paper is organized as follows. In Sec. II the simulation details are given. Results are presented and discussed in Sec. III an conclusions are drawn in Sec. IV.

II. METHODS

The TIP4P water potential has been extensively used for studying supercooled water and it has been recently shown

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also to successfully reproduce the phase diagram of all the stable ice phases of water.[33] MD simulations on this potential[12] estimated the LLCP to be at $T < 200$ K and $P > 70$ MPa. However the exact position has not been clearly determined so far. Ion-ion and ion-water parameters are taken from Jensen and Jorgensen.[34]

The two systems are studied upon supercooling and the range of temperatures spanned goes from $T = 350$ K to $T = 190$ K. The range of densities studied is 0.83 g/cm^3 $\leq \rho \leq 1.10$ g/cm^3. The total number of particles in the simulation box is $N = 256$. In the case of the solution $N = N_{wat} + N_{Na^+} + N_{Cl^-}$ with $N_{wat} = 250$ and $N_{Na^+} = N_{Cl^-} = 3$. The cutoff radius is set to 9.0 Å and the long-range electrostatic interactions are treated by the Ewald summation method. A very recent study proved the importance of the use of Ewald summations[14] in the calculation of the phase diagram especially close to the critical region. Temperature is controlled with the use of the Berendsen thermostat.[35] The longest runs last up to 30 ns and we collected a total of 1848 state points. The total computational time employed is about six central processing unit (CPU) years on a single processor. Simulations were performed using the parallel version of the DL_POLY package.[36]

The temperature of maximum density (TMD) lines have been calculated from the minima of the isochores. The liquid-gas (LG) and the LL limit of mechanical stability (LMS) lines have been calculated considering the points where $(\partial P / \partial \rho)_T = 0$. The position of the LLCP point has been estimated considering the highest temperature of convergence of the isochores in the $P - T$ plane,[13,23] which is also the upper bound of the LL LMS, and also considering the development of a flat region in the isotherms plane and the convergence of the lines of maxima of the isothermal compressibility K_T and of the constant volume specific heat C_V. Generally speaking in fact, the existence of a critical point causes large fluctuations in the region around it. As a consequence above the critical temperature the thermodynamic response functions show loci of extrema that all converge on the Widom line at the critical point.[3]

III. RESULTS AND DISCUSSION

In Fig. 1 we report for bulk TIP4P water the $P - T$ isochores plane, the position of the LLCP of the system, the lines of extrema of thermodynamic response functions, TMD points, and LG LMS line. We locate the position of the LLCP for TIP4P bulk water to be at $T = 190$ K, $P = 150$ MPa, and $\rho = 1.06$ g/cm^3, being in agreement with limits previously estimated for TIP4P bulk water.[12]

In Fig. 2 we report the LLCP, the TMD, and the LG LMS for the bulk TIP4P together with the experimental TMD line. If we now compare the bulk TIP4P TMD and the LLCP with the experiments we note that upon shifting the TIP4P phase diagram of $\Delta T = +31$ K and $\Delta P = -73$ MPa, the TIP4P TMD exactly superposes to the experimental values and the LLCP falls very close to its experimentally hypothesized position. These shifts in pressure and temperatures of the TIP4P phase diagram also agree with the shifts found for ice phases of TIP4P.[33] We also note that the turning point
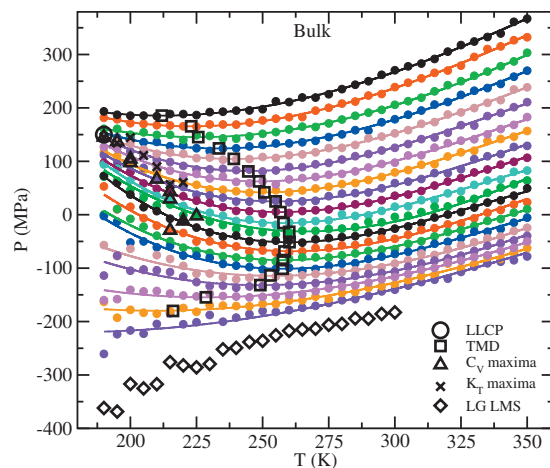

FIG. 1. Isochores for TIP4P bulk water in the $P - T$ plane as obtained from our MD simulations. The maxima of C_V and K_T converge to the LLCP. The TMD points and the LG LMS points are also reported. The difference in the isochores density is $\Delta \rho = 0.01$ g/cm^3, the top density is $\rho = 1.10$ g/cm^3, and the bottom density is $\rho = 0.90$ g/cm^3. Lines are polynomial fits to the simulated state points.

of the shifted TMD line falls around $T = 290$ K and $P = -120$ MPa which is in the experimentally accessible region, above the melting temperature line.[41] Experiments on stretched water have reached $P = -200$ MPa.[42]

In Fig. 3, similar to the bulk, we show the isochores plane for NaCl(aq), the estimated position of the LLCP of the system, the lines of extrema of thermodynamic response functions, the TMD points, and the LL and LG LMS lines. For the same set of densities we observe that the isochores for the solution globally shift to lower pressures with respect to bulk water, with a packing of the isochores close to the LG LMS line. This shift in the thermodynamic plane has been previously observed in solutions.[32,43] We locate the position of the LLCP for NaCl(aq) to be at $T = 200$ K, $P = -50$ MPa, and $\rho = 0.99$ g/cm^3. In the solution it was possible to reach
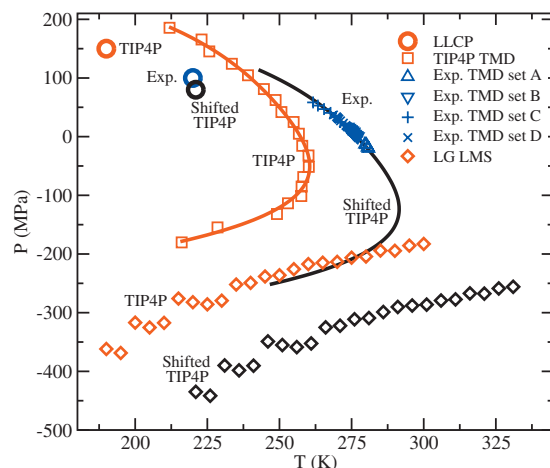

FIG. 2. Thermodynamic loci in the $P - T$ plane of TIP4P bulk water as obtained from our simulations and the same loci shifted to match experimental values. The match is obtained upon applying the shift of $\Delta T = +31$ K and $\Delta P = -73$ MPa. We report the position of the LLCP, the TMD line, and the LG and LMS line. Sources of experimental values: LLCP (Ref. 10), TMD set A (Ref. 37), set B (Ref. 38), set C (Ref. 39), and set D (Ref. 40).
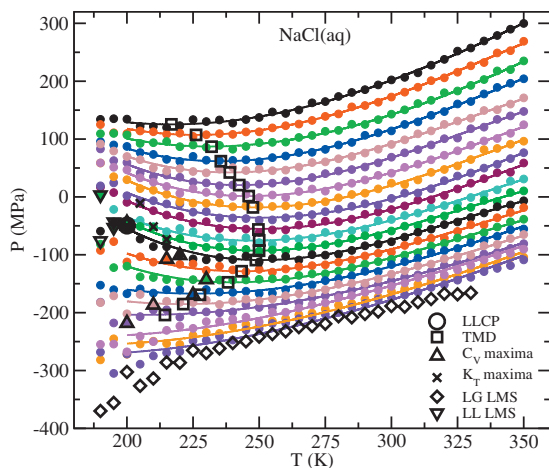
FIG. 3. Isochores for $c=0.67$ mol/kg NaCl(aq) in the $P-T$ plane as obtained from our MD simulations. The maxima of C_V and K_T converge to the LLCP. The TMD points, the LG LMS points, and the LL LMS points are also reported. The difference in the isochores density is $\Delta\rho=0.01$ g/cm^3, the top density is $\rho=1.10$ g/cm^3, and the bottom density is $\rho=0.90$ g/cm^3. Lines are polynomial fits to the simulated state points.

FIG. 5. Thermodynamic loci in the $P-T$ plane of $c=0.67$ mol/kg NaCl(aq) as obtained from our simulations and the same loci shifted in pressure and temperature of the same amount proposed for bulk TIP4P (see Fig. 2), ΔT $=+31$ K and $\Delta P=-73$ MPa. We report the position of the LLCP, the TMD line, and the LG and LL LMS lines. Source of the TMD experimental value: Ref. 26.

equilibrium in our MD simulations for temperature low enough to determine also the two branches of the LL LMS line.

The results obtained directly from simulations for bulk water and for the $c=0.67$ mol/kg NaCl(aq) are summarized in Fig. 4. We also report in the same picture both the experimental TMD line for bulk water and a TMD point at ambient pressure extrapolated for our concentration of salt from experimental data.[26] Both in bulk water and in NaCl(aq) the lines of maxima of the thermodynamic response functions merge in the Widom line very close to the LLCP. The LMS line does not move in the solution with respect to the bulk. The TMD shifts of 10 K to lower temperatures and of ca. 20 MPa to lower pressures. The same shift in temperature is found between the experimental TMD line of bulk water and the TMD point of the solution, at ambient pressure showing
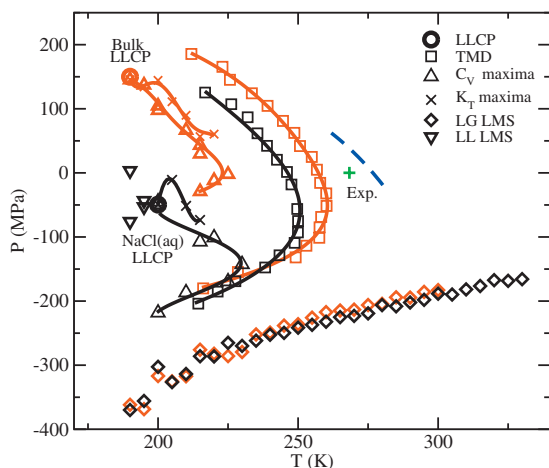

FIG. 4. Comparison of the position of the LLCP and of thermodynamic loci between bulk water (light lines and symbols) and $c=0.67$ mol/kg NaCl(aq) (dark lines and symbols) as obtained from our MD simulation. The lines are meant as guides for the eye. The dashed line is the experimental TMD fitted from data reported in Fig. 2 and the + is the extrapolated experimental TMD point at $P=0.1$ MPa for $c=0.67$ mol/kg NaCl(aq) (Ref. 26).
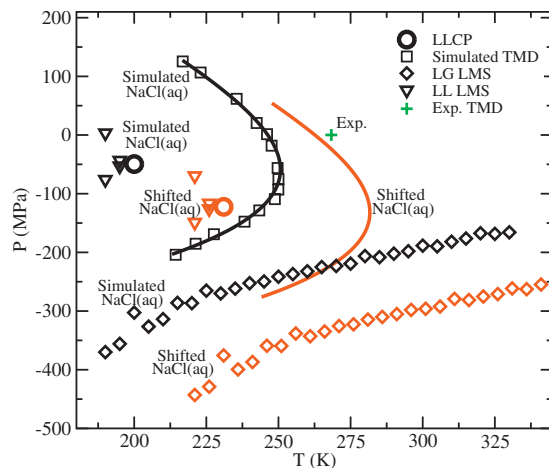
that our MD is able to capture not only the direction but also the magnitude of the shift in temperature found in experiments and confirming that TIP4P is a very good potential for simulating water. We therefore infer that the shift in temperature observed for the LLCP between bulk TIP4P water and TIP4P water in solution is the same as it could be observed in experiments. The LLCP moves in the solution of 10 K toward higher temperatures and shifts in the same direction as TMD in pressure, but of a much larger amount, 200 MPa. This is the signature of the fact that ions stabilize the HDL region consistently shrinking in pressure the LDL region, in agreement with the fact the ions seem to be more favorably solvated in HDL.[29,44] This leads to an extension of the region of existence of the phase where the local structure of water needs less empty spaces.[11] We observed, see Fig. 2, that the TIP4P bulk phase diagram is shifted of $\Delta T \simeq -30$ K and $\Delta P \simeq 70$ MPa with respect to the experimental result.

On the basis of the comparison with the experimental TMD we hypothesize that this shift is preserved for the solution. We report in Fig. 5 the phase diagram of NaCl(aq) as obtained directly from simulations together with the shifted phase diagram. We observe that the experimental TMD value measured for the solution falls very close to the TMD shifted curve of the MD simulation. We predict for the experimental $c=0.67$ mol/kg NaCl(aq) a LLCP at around $T_c \simeq 230$ K and $P_c \simeq -120$ MPa. In experiments on water large negative pressures have been obtained, in particular in NaCl(aq) with concentration $c=1$ mol/kg rupture occurs at $P=-140$ MPa,[42] therefore the negative critical pressure in solution $P_c \simeq -120$ MPa can be reached.

We report in Fig. 6 a schematization of the phase diagrams of both bulk and NaCl(aq) obtained from simulations results shifted to match the experimental values. We infer that these should be the phase diagrams of water and of a $c=0.67$ mol/kg NaCl(aq) aqueous solution as measurable in experiments. We can also see how the LDL region in the solution shrinks with respect to the bulk. On the basis of extrapolation of the data at ambient pressure for other con-
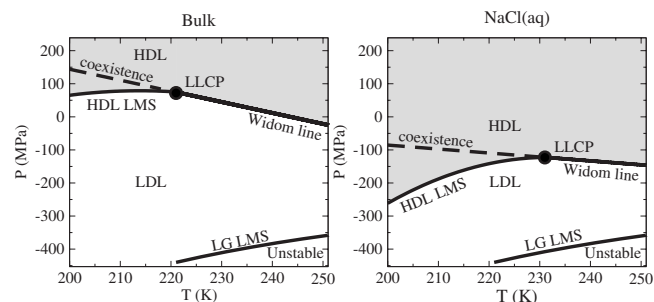
FIG. 6. Schematic HDL-LDL phase diagrams obtained from our MD simulations for bulk water (left panel) and NaCl(aq) (right panel) after applying the shift needed to match experimental values. The LLCP is located at $T \simeq 220$ K and $P \simeq 100$ MPa for bulk water and at $T \simeq 230$ K and $P \simeq -120$ MPa for the $c = 0.67$ mol/kg NaCl(aq).

centrations of NaCl(aq) (Ref. 25) we can estimate that the homogenous nucleation line for our concentration should be shifted of ca. 5 K downward with respect to bulk water (see, e.g., Fig. 1 in Ref. 45). The LLCP in the solution should then be within the supercooled accessible region and a measurement of the LLCP appears possible.

Recent experimental studies on LiCl(aq) have reached the supercooled temperature of $T = 200$ K,[46] showing the existence, also in aqueous solutions, of a fragile to strong dynamical transition typical of glass formers. In water this dynamical transition happens, both in experiments[47] and in simulations,[4,48] upon crossing the Widom line and therefore appears to be related to the possible existence of a LLCP. The Widom line in water, a network forming liquid, appears to play the role of switching line for hopping, favored on the side where water is less dense.[48]

IV. CONCLUSIONS

In this paper we have investigated the possibility to detect the hypothesized LLCP of supercooled water in aqueous solutions of salts. We conclude that the phase diagram of real water is reproducible by TIP4P water upon applying a shift in temperature and pressure that brings the MD TMD to coincide with the experimental values. The LLCP in this shifted diagram falls at $T = 221$ K and $P = 77$ MPa and is located very close to the value hypothesized by Mishima and Stanley,[10] $T \simeq 220$ K and $P \simeq 100$ MPa, corroborating our findings.

Upon applying an analogous shift to the phase diagram of the aqueous solution, we predict the LLCP to be experimentally detectable at $T \simeq 230$ K $P \simeq -120$ MPa for $c = 0.67$ mol/kg NaCl(aq). The comparison of the phase diagrams of the aqueous solution and of bulk water shows that the ions stabilize the HDL phase consequently shrinking the LDL region.

The existence of a LLCP has been connected to a double well effective potential between water molecules.[11] At low enough temperatures the outer and deep subwell drives the system to condense in the LDL phase while the inner subwell at higher enough pressures forces the transition into the HDL phase. If we follow this interpretation our results on the aqueous solution indicate that the effect of the ions is to shift the inner subwell to higher distances so that the HDL phase

becomes stable at lower pressures with respect to bulk water. As a consequence also the TMD line shifts closer to the LLCP. The ions instead do not affect the outer subwell since the LG LMS does not change going from the bulk to the solution. Thus we propose as a valuable route for the experimentalists to solve the issue of the quest of the LLCP of water to perform measurements on aqueous solution of salts.

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