Effect of dissolved salt on the anomalies of water at negative pressure

Alberto Zaragoza,1, 2,a) Chandra Shekhar Pati Tripathi,3, b) Miguel A. Gonzalez,4 José Luis F. Abascal,4 Frédéric Caupin,3, c) and Chantal Valeriania)

1) Departamento Estructura de la materia, física térmica y electrónica, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain
2) Departamento de Ingeniería Física, División de Ciencias e Ingenierías, Universidad de Guanajuato, 37150 León, México
3) Université de Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Villeurbanne, France.
4) Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

(Dated: 28 January 2020)

Adding salt to water at ambient pressure affects its thermodynamic properties. At low salt concentration, anomalies such as the density maximum are shifted to lower temperature, while at large enough salt concentration they cannot be observed any more. Here we investigate the effect of salt on an anomaly recently observed in pure water at negative pressure: the existence of a sound velocity minimum along isochores. We compare experiments and simulations for an aqueous solution of sodium chloride with molality around 1.2 kg m$^{-3}$, reaching pressures beyond $-100$ MPa. We also discuss the origin of the minima in the sound velocity and emphasize the importance of the relative position of the temperatures of sound velocity and density anomalies.

I. INTRODUCTION

While being the most familiar liquid, water is also the most peculiar. It exhibits thermodynamic anomalies, such as a density maximum near 4°C and a compressibility minimum near 46°C at ambient pressure. It also exhibits dynamic anomalies at low temperatures, with the shear viscosity decreasing and the self-diffusion coefficient increasing with applied pressure. Among several theoretical scenarios proposed to explain the origin of water’s anomalies (see Refs. 19 for a review), the second critical point scenario postulates the existence of a phase transition between two distinct metastable liquids terminating at a liquid-liquid critical point (LLCP). One key feature of the second critical point scenario (and also of the singularity free conjecture) is the existence of a maximum in isothermal compressibility along isobars, observed in several molecular dynamics simulations of water.\(^{2, 3, 8, 20, 27, 31, 36, 45}\) Obtaining experimental evidence for such a maximum is a challenging task because it is predicted to lie at large supercooling, very close or even beyond the homogeneous ice nucleation line,\(^{25}\) which is an experimental limit for supercooling real water.

To bypass this limitation, a program was started at the University of Lyon to measure the equation of state of supercooled water at negative pressure. Negative pressure is another metastable state of water, with respect to vapor. Metastability can be terminated by the nucleation of a bubble. However, it has long been recognized that micron-sized fluid inclusions (FI) in quartz provide samples of sufficient cleanliness to reach very large negative pressures, beyond $-100$ MPa, and close to the homogeneous cavitation limit.\(^{26, 29}\) (see also Refs. 10, 12 for reviews on cavitation in water).

The transparent FI samples can be probed by light scattering techniques. In particular, Brillouin spectroscopy, which samples the inelastic interaction between light and density fluctuations in a material, can be used to measure sound velocity $c$. Following this approach, Pallares et al. first observed the existence of minima in $c$ vs. temperature along the quasi-isochore followed by a FI during cooling.\(^{25}\) Based on this observation and on a comparison with molecular dynamics simulations, it was proposed that the $c$ minima along isobars were related to isothermal compressibility $\kappa_T$ maxima along isobars. This long-sought anomaly would become accessible at negative pressure because it would emerge at temperatures above that of homogeneous ice nucleation (which has since been measured at negative pressure using FIs in quartz).\(^{38}\) Further work with other FIs at several densities confirmed the existence of sound velocity minima. Interpolation of the sound velocity data allowed, by thermodynamic integration, to reconstruct the equation of state of water at negative pressure.\(^{23}\) This showed that the temperature of density maxima, increases less and less rapidly with negative pressure, reaching 18.2°C at $-137$ MPa.\(^{23}\) Remarkably, the most recent data suggested the existence of a line of $\kappa_T$ maxima along isobars at the edge of the experimentally accessible region (around $-10$°C and $-100$ MPa). This work also delineated the causal relations between the different lines of anomalies and their relative order. In particular, thermodynamics require that the line of $c$ minima must lie closer to the line of density maxima than the the line of $\kappa_T$ maxima. This means that the line of $c$ minima is easier to access experimentally before ice nucleation occurs.

Two months after publication of Ref. 24, Kim et al. published another report of a maximum in $\kappa_T$, this time near zero pressure. They used fast evaporation of small droplets in vacuum to prepare liquid water at temperatures lower than usual, and pulses from an x-ray laser to measure the static structure factor $S(q)$ at wavenumber $q$. Extrapolating $S(q)$ to $q = 0$ yields a quantity proportional to $\kappa_T$. Kim et al. con-

---

a) These authors contributed equally.
b) Electronic mail: frederic.caupin@univ-lyon1.fr
c) CSPT now at: Department of Physics, Institute of Science, Banaras Hindu University, Varanasi-221005, India.
cluded that a $\kappa_T$ maximum exists at 229 K. However, extracting $\kappa_T$ requires calculating the droplet temperature, and an extrapolation of density data. This extrapolation of density data and the existence of a $\kappa_T$ maximum have been later debated \cite{13,14}, and the accuracy of the reported temperature put into question \cite{15,16}. Nevertheless, if it exists, the $\kappa_T$ maximum near zero pressure would be compatible with the $\kappa_T$ maxima reported at negative pressure. We also note that a recent 2-state model for water \cite{17} which assumes the existence of a LLCP is able to quantitatively reproduce many thermodynamic measurements both at positive and negative pressure.

In order to shed light on the origin of water’s anomalies, more data are highly needed. One possible route is to add a solute to water. This has the effect of modifying the phase diagram and moving or suppressing the lines of anomalies. A solute also shifts the ice nucleation line to lower temperatures. A good candidate is salt (sodium chloride NaCl). Its effect on the anomalies of water has been studied in experiments and simulations \cite{18,19}. It is predicted that the LLCP seen in simulations of pure water shifts to higher temperature and lower, possibly negative, pressure. As the line of $\kappa_T$ maxima emanates from the LLCP, it is also shifted in the same direction. However, the line of density maxima is shifted to lower temperatures. Based on thermodynamic reasoning \cite{20}, a line of $c$ minima must exist between the lines of $\kappa_T$ and density maxima in the solution. However, its location with respect to the line of $c$ minima in pure water cannot be predicted by thermodynamic arguments only. Here we address this question by a combined experimental and simulation study of an aqueous solution of sodium chloride at negative pressure. Numerical data and the existence of a $c$ maximum have been later de-

### II. NUMERICAL RESULTS

#### A. Simulation details

Molecular dynamics simulations were carried out with GROMACS 2016.4 \cite{21,22}, using 91 Na$^+$ and Cl$^-$ ions and 3818 water molecules, which corresponds to a molarity of 1.323 M. Water was simulated using the TIP4P/2005 model \cite{23}, which consists of a Lennard-Jones and a Coulomb term, while NaCl ions were simulated using two different models: Joung-Cheatham \cite{24} and the so called Madrid model \cite{25}. Water-ions interactions are reported in table I. When simulated water, we truncated the Lennard-Jones (LJ) potential at 9.5 Å, adding standard long-range corrections to the LJ energy, and using Ewald sums (with PME technique) \cite{26} for the calculation of the long-range electrostatic forces, with a real space cut-off at 9.5 Å. Periodic boundary conditions were applied in all directions. We set the time step to 1 fs and simulate every temperature for at least 200ns (lower temperatures required longer simulations reaching up to 500ns). In order to keep temperature and pressure constant, we used a Nose-Hoover thermostat \cite{27,28} and a Parrinello-Rahman barostat \cite{29,30} with a relaxation time set to 1 ps for both.

#### TABLE I. Interaction parameters for the force-fields used in this work: Joung-Cheatham - TIP4P/2005, and Madrid Model - TIP4P/2005

|                | Joung-Cheatham - TIP4P/2005 | Madrid model - TIP4P/2005 |
|----------------|-----------------------------|---------------------------|
| $\sigma$/nm    | Na$^+$-Na$^+$: 0.2135938     | Na$^+$-Na$^+$: 0.221737    |
|                | Cl$^-$-Cl$^-$: 0.4830453     | Cl$^-$-Cl$^-$: 0.484906    |
|                | Na$^+$-Cl$^-$: 0.3494996     | Na$^+$-Cl$^-$: 0.290512    |
|                | O-O: 0.315890                | O-O: 0.315890              |
|                | Na$^+$-O: 0.2659219          | Na$^+$-O: 0.251338         |
|                | Cl$^-$-O: 0.399445           | Cl$^-$-O: 0.426867         |

We have performed $NVT$ (where $N$ is the number of particles, $V$ the volume, and $T$ the temperature) simulations to calculate pressure $P$ and isochoric heat capacity $C_V$, using:

$$C_V = \frac{\langle U^2 \rangle - \langle U \rangle^2}{k_B T^2},$$

where $\langle U \rangle$ is the energy and $k_B$ is the Boltzmann constant. We have also performed $NPT$ simulations to calculate isobaric heat capacity $C_P$ and isothermal compressibility $\kappa_T$, using:

$$C_P = \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2},$$

$$\kappa_T = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle k_B T},$$

where $H$ is the enthalpy. Finally, the speed of sound $c$ was obtained via the Newton-Laplace formula:

$$c = \sqrt{\frac{C_P}{C_V}} \frac{1}{\kappa_T \rho},$$

where $\rho$ is the density of the liquid.

#### B. Comparison between Joung-Cheatham and Madrid models

We first compare the pressure computed along the $\rho = 996.5$ kg m$^{-3}$ isochore for the two models (Fig. I). This density value was chosen to obtain a pressure with the Madrid model close to the one estimated for the experiment (see Section III). The two models give similar results, with the Madrid
model yielding a pressure shifted up by around 30 MPa compared to the Joung-Cheatham model. Both isochores show a minimum around 260 − 263 K, which corresponds to a point along the line of density maxima of the solution. The data for each extrema observed in the simulations are given in Table III.

In the following, we compare other thermodynamic properties for the two models. We also compare the results for the Madrid model with those for pure TIP4P/2005 water, but at density values chosen to follow the same temperature-pressure path as shown in Fig. 1. This is conveniently done using the two-state equation of state for TIP4P/2005 presented by Biddle et al. in Ref. 8, given that this equation of state is valid at negative pressure and up to 320 K.

Figure 2 displays heat capacity at constant volume (panel a) and constant pressure (panel b) for the two models. The results are very close to each other. Both models show a mild maximum in \( C_V \) and \( C_P \) around 246 − 247 K, with a peak being slightly higher for the Madrid model (see also Table III). When comparing the results for pure TIP4P/2005 and for the Madrid model along the same \( T − P \) path (Fig. 1), adding salt to water reduces \( C_P \) and \( C_V \) and makes their peaks less pronounced.

Figure 3 displays the isothermal compressibility for the two models as compared to water. The results are again close to each other. Both models show a weak maximum in \( \kappa_T \) around 307 − 308 K, with the peak being slightly higher for the Madrid model (see also Table III). When comparing the results for pure TIP4P/2005 and for the Madrid model along the same \( T − P \) path (Fig. 1), adding salt to water decreases \( \kappa_T \) making the maximum less pronounced.

Finally Fig. 4 displays the calculated sound velocity. The two models for salty water give similar results, both with a minimum in \( c \) around 293 − 296 K (see Table III). The sound velocity is shifted to higher values in the case of the Joung-Cheatham model. When comparing the results for pure TIP4P/2005 and for the Madrid model along the same \( T − P \) path (Fig. 1), adding salt to water makes the sound velocity minimum shallower.

From this analysis we conclude that the two NaCl models yield qualitatively identical and quantitatively close results. The most noticeable difference is the magnitude of the pres-

### Table II. Extrema values of the properties along the isochore at \( \rho = 996.5 \text{kg m}^{-3} \) for Joung-Cheatham and Madrid models at 1.323 M.

| Quantity | \( T \), K | \( P \), MPa | Value |
|----------|------------|-------------|-------|
| min. \( P \) | 260        | -1515       |       |
| max. \( C_V \) | 246        | -149.2 98.8 J mol\(^{-1} \) K\(^{-1} \) |       |
| max. \( C_P \) | 250        | -149.6 96.3 J mol\(^{-1} \) K\(^{-1} \) |       |
| max. \( \kappa_T \) | 307        | -127.1 5.310\(^{-4} \) MPa\(^{-1} \) |       |
| min. \( c \) | 293        | -124.1 1390 m s\(^{-1} \) |       |

| Quantity | \( T \), K | \( P \), MPa | Value |
|----------|------------|-------------|-------|
| min. \( P \) | 263        | -122.3      |       |
| max. \( C_V \) | 247        | -118.3 99.5 J mol\(^{-1} \) K\(^{-1} \) |       |
| max. \( C_P \) | 248        | -119.1 98.1 J mol\(^{-1} \) K\(^{-1} \) |       |
| max. \( \kappa_T \) | 308        | -100.4 5.410\(^{-4} \) MPa\(^{-1} \) |       |
| min. \( c \) | 296        | -98.8 1357 m s\(^{-1} \) |       |
FIG. 3. Isothermal compressibility along the isochore at $\rho = 996.5 \text{ kg m}^{-3}$ for Joung-Cheatham (red stars) and Madrid model (blue circles) at 1.323 M. The green dashed curve shows the values for pure TIP4P/2005 water calculated from the EOS from Ref. 8 along the same temperature-pressure path as followed along the isochore.

FIG. 4. Sound velocity computed along the isochore at $\rho = 996.5 \text{ kg m}^{-3}$ for Joung-Cheatham (red stars) and Madrid Model (blue circles) at 1.323 M. The green dashed curve shows the values for pure TIP4P/2005 water calculated from the EOS from Ref. 8 along the same temperature-pressure path as followed along the isochore with the Madrid model.

III. EXPERIMENTAL RESULTS

A. Experimental details

The sample is a natural quartz fragment from the Mont Blanc massif in the French Alps. We have selected a FI containing salt and able to reach a large negative pressure. This particular FI has already been studied, but only above 100 °C, in Ref. 17 (sample FI4), which presented a method for using Brillouin spectroscopy as a paleothermometer. Here we have extended the measurements to lower temperatures and pressure reached along the studied isochore. For the remainder of the article, we will present only results obtained with the Madrid model.

B. Comparison between pure and salty water

We now present the results obtained with the natural salty sample and compare them with those previously obtained with a synthetic pure water sample.24

Figure 6 displays the pressure reached along the experimental path. Rather than a perfect isochore, because of thermal expansion and elasticity of the quartz matrix, the experiment follows a quasi-isochore, with a typical density variation of a fraction of a percent. In the case of the salty sample, the pressure along the quasi-isochore can only be estimated, as it involves the extrapolation of an equation of state for NaCl solutions at positive pressure (AlGhafri et al., see Appendix A for details). The pressure values for the salty sample should there-
Therefore be taken with caution. In contrast, in the case of the pure water sample, the pressure is calculated using the experimental equation of state at negative pressure obtained in Ref. 24 by thermodynamic integration of a set of speed of sound data at various temperatures and densities. The pressure is therefore more reliable in the pure water case. For the present study, we have taken the data from one of the samples studied in Ref. 24, which we selected because its pressure-temperature path was the closest to the one estimated for the present salty sample. This allows a more direct comparison between pure and salty water.

Figure 7 displays the sound velocity obtained from Brillouin measurements on the pure and the salty samples. When a bubble is present in the fluid inclusion, it is at the liquid-vapor equilibrium. The sound velocity measured under this condition (shown with empty symbols) is in excellent agreement with the values expected from standard measurements along true isochores, interpolation and thermodynamic integration allowed to construct an experimental equation of state. Using this EoS, it was shown that the minimum in sound velocity vs. density dependence of the sound velocity (see Ref. 33, in particular Fig. 4, and Ref. 44, in particular Fig. 1). In contrast, the sound velocity for the salty sample always remain below the liquid-vapor equilibrium values in the temperature range studied.

IV. DISCUSSION

In this section we use the comparison between experiments and simulations to discuss the possibility to experimentally observe at negative pressure anomalies in salty water equivalent to those previously observed in pure water24.

A. Comparison between simulations and experiments

The simulation results reported in Fig. 4 were for perfect isochores, whereas experiments follow a quasi-iscohere (see Section III.B). In the case of pure water, this was carefully taken into account using quartz properties and an iterative procedure23,33. As samples were studied along different quasi-isochores, interpolation and thermodynamic integration allowed to construct an experimental equation of state. Using this EoS, it was shown that the minimum in sound velocity vs. temperature observed along quasi-isochores remains present along true isochores.

In the case of salty water, the question arises if the difficulty to conclude about the existence of a minimum in the
measured sound velocity data (Fig. 7) might be due to the thermodynamic path. One possibility could be that a stronger minimum exists along an isochore, and becomes smeared out along the quasi-isochore which is actually measured. Unfortunately, data measured along only one quasi-isochore are not sufficient to construct an experimental EoS with enough accuracy and to give the sound velocity along a true isochore. Still, the above possibility can be tested with simulations. We repeated the simulations with TIP4P/2005 for water and Madrid model for NaCl at 1.323 M, along the $\rho = 996.5 \text{ kg m}^{-3}$ isochore and a quasi-isochore, corresponding to the experimental values for the densities. Fig. 8 shows that the pressure along the experimental and simulated quasi-isochores are in good agreement. Fig. 9 shows the comparison between sound velocity simulated along the isochore and the quasi-isochore. The changes are small but systematic. They make the sound velocity minimum less pronounced along the quasi-isochoric path than along the isochoric path, but near the minimum the differences are very small.

In the case of experiment, we conclude that it is unlikely that measuring along a true isochore (if this were possible) rather than along a quasi-isochore would qualitatively change our results. Fig. 10 shows the comparison of the sound velocity between experiments and simulations. The rather close agreement along the quasi-isochore suggests that a minimum could exist in experiments, although, as noted in Section III, the scatter of experimental data does not allow to reach a clear conclusion. To decide about the existence or absence of a minimum in experiments, a critical step forward would be to acquire more data at lower temperature. In fact, the sample remains in the fluid state at lower temperature, as confirmed with Raman spectroscopy for instance. Unfortunately, we were not able take sound velocity data below 258.15 K because sound attenuation then becomes too strong and we loose the Brillouin signal.

### B. Origin of the minima in sound velocity

A major question in the context of the debate about the origin of water’s anomalies is the origin of the minima in sound velocity. In the case of pure water, such minima have been observed both in experiments and simulations. In Ref. 24, several first-principle, thermodynamic relations were derived, and their consequences on the different lines of anomalies were studied. In particular, it was shown that, if a LLCP exists, a line of sound velocity minima along isobars ($L_m|P$) must emanate from this critical point. This makes the existence of a $L_m|P$ a necessary (but not sufficient) condition for the second critical point scenario to be valid. If a LLCP exists in pure water, it will be preserved by the addition of a solute. However, the critical behaviour differs: the osmotic susceptibility, not the isothermal compressibility, diverges at the LLCP, from which a line of osmotic susceptibility maxima emerges. Still, for sufficiently low concentrations, a line of isothermal compressibility maxima will be preserved; the smaller the solute concentration, the closer the lines of isother-
mal compressibility and osmotic susceptibility maxima. We thus expect that the existence of a LLCP in pure water would still cause a line of sound velocity minima in salty water, with minima that would become less and less pronounced with the increase of salt concentration. This is consistent with what is observed in our simulations (see Section IIIB).

However, Altabet et al. recently investigated another possible source of sound velocity minima along isochores: the case of a liquid–vapor spinodal exhibiting a maximum in its density vs. temperature. These authors showed that “a maximum spinodal density in water results in a locus of maximum compressibility and a minimum speed of sound that are independent from any influence of a LLCP”. They reproduced our previous results for the sound velocity minima along two isochores obtained with TIP4P/2005, and obtained more minima for isochores at lower densities. They argued that “the $\kappa_T^{\max}$ [line of maxima in $\kappa_T$ along isochores] is not the negative pressure extension of a line emanating from higher pressure. Instead, it is due to the peculiar behavior of water’s spinodal in its $T - \rho$ phase diagram and originates at negative pressure.”

A question thus arises about the relevance of our observations to the debate about the existence of a LLCP. In case of pure water, the answer to this subtle question can be found by looking at the lines of extrema for TIP4P/2005, which can be plotted to their full extent in Fig. [11] thanks to the available parameterization of the simulation data with a two-state model. As explained in details in the Supporting Information of Ref. [24], there are thermodynamic requirements. For a quantity $X$, let us call $Lm_X|Y$ and $LM_X|Y$ the loci of $X$ minima and maxima along a constant $Y$ path. A $Lmc|P$ must emanate from the LLCP. Let us call M the point at which the temperature of maximum density (TMD) reaches its maximum. At M, an extremum in sound velocity along isobars must be reached. If this extremum is a minimum, the $Lmc|P$ extends from the LLCP to temperatures above the TMD maximum. If, instead, the extremum at M is a sound velocity maximum, then the $Lmc|P$ will stop at a temperature lower than that of M, and will merge with a $Lmc|P$. TIP4P/2005 is a borderline case, with the $Lmc|P$ connecting with the $Lmc|P$ nearly exactly at M. Coming back to the argument by Altabet et al., we see in Fig. [11] that they plotted in their Fig. 4 only the high temperature part of the $LMc|\rho$. Upon cooling, it becomes a line of minima in $\kappa_T$ along isochores, $Lmx_T|\rho$, and upon further cooling, once again a $LMcT|\rho$. The low temperature $LMcT|\rho$ eventually tracks the low temperature part of the $Lmc|\rho$, the two lines passing to the left of the LLCP, as they should. At low temperature, $LMcT|\rho$ and $Lmc|\rho$ become nearly parallel to $LMcT|\rho$ and $Lmc|\rho$, respectively, the two latter lines terminating at the LLCP. We see that, if at high temperature $LMcT|\rho$ and $Lmc|\rho$ are indeed caused by the spinodal, at low temperature they are caused by the LLCP.

The key to recognize the possible cause for these anomalies is to scrutinize their location relative to the TMD. To the right of (i.e. at temperatures above) the TMD they are influenced by the spinodal, whereas to the left of (i.e. at temperatures below) the TMD they are related to the LLCP. Altabet et al. are right about the spinodal origin of the minimum sound velocity along the 933.2 kg m$^{-3}$ isochore for TIP4P/2005 water, as it lies to the right of the corresponding TMD. In our previous work, we simulated this particular isochore to match the experimental density, but we were not aware of the issue at that time. However, the experimental equation of state deduced from our measurements puts the observed minima in sound velocity along isochores (for 6 samples at different densities, including 933.2 kg m$^{-3}$) to the left of the TMD. This also explains why corresponding sound velocity minima along isobars are observed in the experimental EoS (see Fig. 2 of Ref. [24]), which would not be the case if they were located to the right of the TMD. The experimental findings thus realize the necessary (but not sufficient) condition for a LLCP to exist in real water.

Now that, thanks to Altabet et al., we have realized the importance of the TMD location, we can wonder if we would have been able to provide a better comparison between experiments and simulations. For TIP4P/2005, we selected the same density values for the simulation as in the experiment, which yielded a good agreement for the sound velocity, but the resulting minima along isochores lied to the right of the TMD. Simulating TIP4P/2005 isochores at a sufficiently higher density would place the sound velocity minimum to the left of the TMD, but the agreement with experimental values for sound velocity and pressure would decrease. This issue arises from the fact that, for TIP4P/2005, the TMD changes slope around $-80$ MPa and $\rho \approx 955$ kg m$^{-3}$, whereas in experiments, the TMD keeps a negative slope to more negative pressures (at least $-137$ MPa), and a sound velocity minimum is observed only for $\rho < 951$ kg m$^{-3}$. Therefore, we may consider using another force field to make the comparison more meaningful.

In a recent work, Singraber and Dellago have compiled the available TMD lines and added two new ones based on ab initio trained high-dimensional neural network potentials. We
FIG. 12. Pressure of pure water as a function of temperature computed for different models presented in Ref. 12. Green symbols represent the experimental measurements for pure water at negative (circles) and positive pressures (triangles). The purple dashed curve shows the location of experimental minima along isochores.

compare them to the experimental location of the \( \text{Lm}_c \) and \( \text{Lm}_c / \rho \) in Fig. 12. The experimental lines lie in an appropriate position relative to the simulated TMDs only for TIP4P/2005 and BLYP-D3. However, the TMD for BLYP-D3 is not satisfactory as it does not reach positive pressure. Therefore TIP4P/2005 is the best possible choice among the potentials compared in Fig. 12.

Turning to simulations of salty water with TIP4P/2005 for water and the Madrid model for salt, we chose a density which gives a pressure close to the experimental one (Fig. 13). We have also computed the TMD from several NVT simulations at the same NaCl concentration. The result is displayed in Fig. 13. The minimum in sound velocity along the simulated isochore lies to the right of the TMD, and is therefore due to the spinodal. We cannot conclude for the experimental case, as we are neither sure about the existence of the minimum, nor about the location of the TMD. This highlights the need for a more systematic study with measurements of samples at various densities. This will allow determining the experimental equation of state, and, if a minimum is confirmed, elucidate its location with respect to the TMD.

**ACKNOWLEDGMENTS**

We thank Mikhail A. Anisimov for helpful discussions on critical phenomena in solutions, and Christoph Dellago and Andreas Singraber for providing the data used to plot Fig. 12. C.S.P.T. and F.C. acknowledge funding by the European Research Council under the European Community’s FP7 Grant Agreement 240113. CV acknowledges fundings from the Spanish Ministry of Education FIS2016-78847. AZ was funded by CONACYT (PhD fellowship), where MAG by the Spanish Ministry of Education (Juan de la cierva fellowship).

**Appendix A: Obtaining sound velocity from the Brillouin spectra**

The refractive index is needed to obtain the sound velocity from the Brillouin shift. We calculate the refractive index \( n \) as follows. We assume the validity of the Gladstone-Dale relation, \( n(T, m) = 1 + K(m) \rho(T, m) \) where \( \rho(T, m) \) is the density at temperature \( T \) and molality \( m \). We calculate the constant \( K(m = 1.20) \) using interpolated values at 20°C for the density and refractive index (at 589 nm). To compute \( n(T, m = 1.20) \) at various temperatures, we use the correlation of density measurements for NaCl solutions in the range 25 to 200 °C, 0 to 6 mol kg\(^{-1}\), and 0.1 to 68.5 MPa. For simplicity we took \( P = 0.1 \text{ MPa} \) when a bubble was present in the inclusion. Note that we used the refractive index tabulated at 589 nm, whereas the experiment is carried out at 532 nm. In our experiments, this difference was not significant as we checked by measuring Brillouin spectra as a function of temperature and molality for NaCl solutions contained in capillaries (Fig. 4b of Ref. 12). As the exact solute present in the natural sample is unknown, we did not attempt to repeat the procedure at the correct wavelength. In future work, when synthetic samples containing only NaCl and water will be used, a more accurate analysis would be in order.

The Brillouin spectra are analyzed with the viscoelastic model, convoluted with the instrumental response function (see Refs. 12–14 for details). All fits are excellent with a typical reduced \( \chi^2 \) around 1 (at most 1.7). We use a constant sound velocity at infinite frequency \( c_\infty = 3000 \text{ m s}^{-1} \), as was done for pure water. The analysis yields the sound velocity at zero frequency \( c_0 \). All results for \( c_0 \) are then multiplied by a common correction factor 1.01029. The correction factor was determined from the ratio between the expected value for pure water and the raw \( c_0 \) obtained for pure water in a capillary. This includes possible biases in the scan amplitude and in the definition of the collection angle. No significant variation of the correction factor was observed be-
between 20 and 60 °C, therefore the average ratio was used as a constant correction factor. In the regime of the experiment, \((c_0/c_{\infty})^4(2\pi\Delta f_0\tau)^2 \ll 1\), where \(\Delta f_0\) is the Brillouin frequency shift and \(\tau\) the viscoelastic relaxation time), the correction for \(c_0\) simply amounts to multiplying all raw results for \(c_0\) by a constant factor 1.01029.

For the monophasic inclusions, a first analysis is carried out assuming the density remains constant, equal to \(\rho_0 = 987.3 \text{kg m}^{-3}\) determined from the homogenization temperature \(T_h\). According to the Gladstone-Dale relation, the refractive index is also constant. Then two corrections are needed to account for the change in volume of the inclusion. The first arises from the thermal expansion of quartz, the second from its elasticity. A rough estimate of the pressure is obtained by extrapolating to negative pressure the correlation from Al-Ghafari et al. The correlation was developed for pressures in the range 0.1 to 68.5 MPa, but it is well behaved to large negative pressures. At each temperature, the pressure in the inclusion is estimated as the extrapolated pressure \(P\) at which the density would be equal to \(\rho_0\). A new density \(\rho_{\text{new}}\) is then obtained accounting for quartz expansion and stretching, using:

\[
\rho_{\text{new}} = \rho_0 \left(1 + \alpha_v (T - T_h) + \frac{1 + \nu}{1 - 2\nu} \frac{P}{B} \right)^{-1}, \quad (A1)
\]

where \(\alpha_v\), \(\nu\) and \(B\) are the volume expansion coefficient, Poisson coefficient, and bulk modulus of quartz, respectively. Values are given in Ref. 2.

The Gladstone-Dale relation gives the refractive index corresponding to \(\rho_{\text{new}}\), which is then used to obtain the value of \(c_0\) corrected for non-isochoric effects. These corrections give only minor changes to the sound velocity (at most 2.5 m/s or 0.19 % at -15 °C, to compare to our 0.4 % uncertainty). Note that, in previous work on pure water, the measured sound velocity itself was used to obtain an experimental equation of state at negative pressure, and hence the pressure in the inclusions. The procedure was iterated until convergence was achieved (which takes only 2 to 3 iterations). In view of the present data limited to one sample, and on the very moderate correction calculated, we choose not to use the iterative procedure and to limit the density correction to the first-order approximation presented above. As the possible resulting error is on the density correction, we expect the values of density, refractive index and sound velocity to be rather accurate. In contrast, the pressure itself, displayed in Fig. 6, is more sensitive to the choice of extrapolation for the equation of state.

**BIBLIOGRAPHY**

1. J. L. Abascal and C. Vega. A general purpose model for the condensed phases of water: Tip4p/2005. *The Journal of chemical physics*, 123(23):234505, 2005.

2. J. L. F. Abascal and C. Vega. Widom line and the liquid–liquid critical point for the tip4p/2005 water model. *The Journal of Chemical Physics*, 133(23):234502, 2010.

3. J. L. F. Abascal and C. Vega. Note: Equation of state and compressibility of supercooled water: Simulations and experiment. *The Journal of Chemical Physics*, 134(18):186101, 2011.

4. A. Al-Ghafari, G. C. Maitland, and J. M. Trusler. Densities of aqueous mgcl2 (aq), cac2 (aq), kcl (aq), clcl (aq), alcl3 (aq), and (0.964 nacl+ 0.136 kcl)(aq) at temperatures between (283 and 472) k, pressures up to 68.5 mpa, and molalities up to 6 mol- kg⁻¹. *Journal of Chemical & Engineering Data*, 57(4):1288–1304, 2012.

5. Y. E. Altabet, R. S. Singh, F. H. Stülinger, and P. G. Debenetti. Thermodynamic anomalies in stretched water. *Langmuir*, 33(42):11771–11778, 2017.

6. D. G. Archer and R. W. Carter. Thermodynamic Properties of the NaCl + H₂O System. 4. Heat Capacities of H₂O and NaCl(aq) in Cold-Stable and Supercooled States. *J. Phys. Chem. B*, 104(35):8563–8584, Sept. 2000.

7. A. Benavides, M. Portillo, V. Chamorro, J. Espinosa, J. Abascal, and C. Vega. A potential model for sodium chloride solutions based on the tip4p/2005 water model. *The Journal of chemical physics*, 147(10):104501, 2017.

8. W. Biddle, R. S. Singh, E. M. Sparano, F. Ricci, M. A. González, C. Valeriani, J. L. Abascal, P. G. Debenetti, M. A. Anisimov, and F. Caupin. Two structure-thermodynamic models for the tip4p/2005 model of water covering supercooled and deeply stretched regions. *The Journal of chemical physics*, 146(3):034502, 2017.

9. F. Caupin. Liquid-vapor interface, cavitation, and the phase diagram of water. *Phys. Rev. E*, 71(5):051605, May 2005.

10. F. Caupin. Escaping the no man’s land. Recent experiments on metastable liquid water. *J. Non-Cryst. Solids*, 407:441–448, Jan. 2015.

11. F. Caupin and M. A. Anisimov. Thermodynamics of supercooled and stretched water: Unifying two-structure description and liquid-vapor spinodal. *The Journal of chemical physics*, 151(3):034503, 2019.

12. F. Caupin and E. Herbert. Cavitation in water: A review. *Comptes Rendus Phys.*, 7(9-10):1000–1017, NOV-DEC 2006.

13. F. Caupin, V. Holten, C. Qiu, E. Guillerm, M. Wilke, M. Frenz, J. Teixeira, and A. K. Soper. Comment on “Maxima in the thermodynamic response and correlation functions of deeply supercooled water”. *Science*, 360(6390):eaat1634, May 2018.

14. D. Corradini and P. Gallo. Liquid–Liquid Coexistence in NaCl Aqueous Solutions: A Simulation Study of Concentration Effects. *J. Phys. Chem. B*, 115(48):14161–14166, Dec. 2011.

15. D. Corradini, M. Rovere, and P. Gallo. A route to explain water anomalies from results on an aqueous solution of salt. *J. Chem. Phys.*, 132(13):134508–134508–5, Apr. 2010.

16. M. El Mekki Azouzi, C. Ramboz, J.-F. Lenain, and F. Caupin. A coherent picture of water at extreme negative pressure. *Nat. Phys.*, 9(1):38–41, Jan. 2013.

17. M. El Mekki-Azouzi, C. S. P. Tripathi, G. Pallares, V. Gardien, and F. Caupin. Brillouin spectroscopy of fluid inclusions proposed as a paleothermometer for subsurface rocks. *Scientific reports*, 5:13168, 2015.

18. U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen. A smooth particle mesh ewald method. *The Journal of Chemical Physics*, 103(19):8577–8593, 1995.

19. P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. Mettersson. Water: A Tale of Two Liquids. *Chem. Rev.*, 116(13):7463–7500, July 2016.

20. M. A. González, C. Valeriani, F. Caupin, and J. L. F. Abascal. A comprehensive scenario of the thermodynamic anomalies of water using the tip4p/2005 model. *The Journal of Chemical Physics*, 145(5):054505, 2016.

21. C. Goy, M. A. C. Potezna, S. Dedera, M. Tomut, E. Guillerm, A. Kalinin, K.-O. Voss, A. Schottelius, N. Petridis, A. Prosvetov, G. Tejeda, J. M. Fernández, C. Trautmann, F. Caupin, U. Glasmacher, and R. E. Grisenti. Shrinking of Rapidly Evaporating Water Microdroplets Reveals their Extreme Supercooling. *Phys. Rev. Lett.*, 120(1):015501, Jan. 2018.

22. W. M. Haynes. *CRC handbook of chemistry and physics*. CRC press, 2014.

23. B. Hess, C. Kutzner, D. Van Der Spoel, and E. Lindahl. Gromacs 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. *Journal of chemical theory and computation*, 4(3):435–447, 2008.

24. V. Holten, C. Qiu, E. Guillerm, M. Wilke, J. Ricka, M. Frenz, and F. Caupin. Compressibility Anomalies in Stretched Water and Their Interplay with Density Anomalies. *J. Phys. Chem. Lett.*, 8(22):5519–5522, Nov. 2017.

25. V. Holten, J. V. Sengers, and M. A. Anisimov. Equation of State for Supercooled Water at Pressures up to 400 MPa. *J. Phys. Chem. Ref. Data*, 9.
I. S. Joung and T. E. Cheatham III. Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations. *The journal of physical chemistry B*, 112(30):9020–9041, 2008.

K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, et al. Maxima in the thermodynamic response and correlation functions of deeply supercooled water. *Science*, 358(6370):1589–1593, 2017.

K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, K. H. Nam, T. Katayama, and A. Nilsson. Response to Comment on “Maxima in the thermodynamic response and correlation functions of deeply supercooled water”. *Science*, 360(6390):eaat1729, May 2018.

G. Menzl, M. A. Gonzalez, P. Geiger, F. Caupin, J. L. F. Abascal, C. Valeriani, and C. Dellago. Molecular mechanism for cavitation in water under tension. *Proc. Natl. Acad. Sci.*, 113(48):13582–13587, Nov. 2016.

F. J. Millero, G. K. Ward, and P. V. Chetirkin. Relative sound velocities of sea salts at 25 c. *The Journal of the Acoustical Society of America*, 61(6):1492–1498, 1977.

M. Motakabbir K.A. and Berkowitz. Isothermal compressibility of spc/e water. *J. Phys. Chem.*, 94:8359–8362, 1990.

S. Nosé. A unified formulation of the constant temperature molecular dynamics methods. *The journal of chemical physics*, 81(1):511–519, 1984.

G. Pallares, M. A. Gonzalez, J. L. F. Abascal, C. Valeriani, and F. Caupin. Anomalies in bulk supercooled water at negative pressure. *Proceedings of the National Academy of Sciences*, 111(22):7936–7941, 2014.

G. Pallares, M. A. Gonzalez, J. L. F. Abascal, C. Valeriani, and F. Caupin. Equation of state for water and its line of density maxima down to -120 MPa. *Phys. Chem. Chem. Phys.*, 18(8):5896–5900, Feb. 2016.

M. Parrinello and A. Rahman. Polymorphic transitions in single crystals: A new molecular dynamics method. *Journal of Applied Physics*, 52(12):7182–7190, 1981.

H. L. Pi, J. L. Aragones, C. Vega, E. G. Noya, J. L. Abascal, M. A. Gonzalez, and C. McBride. Anomalies in water as obtained from computer simulations of the tip4p/2005 model: density maxima, and density, isothermal compressibility and heat capacity minima. *Molecular Physics*, 107(4-6):365–374, 2009.

P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley. Phase behaviour of metastable water. *Nature*, 360(6402):324–328, Nov. 1992.

C. Qiu, Y. Krüger, M. Wilke, D. Marti, J. Ricka, and M. Frenz. Exploration of the phase diagram of liquid water in the low-temperature metastable region using synthetic fluid inclusions. *Phys. Chem. Chem. Phys.*, 18(40):28227–28241, Oct. 2016.

F. Roedder. Metastable Superheated Ice in Liquid-Water Inclusions under High Negative Pressure. *Science*, 155(3768):1413–1417, Mar. 1967.

S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley. Singularity-free interpretation of the thermodynamics of supercooled water. *Phys. Rev. E*, 53:6144–6154, Jun 1996.

J. M. L. Sengers. Critical behavior of fluids: concepts and applications. In *Supercritical Fluids*, pages 3–38. Springer, 1994.

L. P. Singh, B. Issenmann, and F. Caupin. Pressure dependence of viscosity in supercooled water and a unified approach for thermodynamic and dynamic anomalies of water. *Proc. Natl. Acad. Sci.*, 114(17):4312–4317, Apr. 2017.

A. Singraber, T. Morawietz, J. Behler, and C. Dellago. Density anomaly of water at negative pressures from first principles. *Journal of Physics: Condensed Matter*, 30(25):254005, 2018.

W. Wagner and A. Pruß. The iapws formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *Journal of physical and chemical reference data*, 31(2):387–535, 2002.

L. Xu, P. Kumar, S. Buldyrev, S.-H. Chen, P. Poole, F. Sciortino, and H. Stanley. Relation between the widom line and the dynamic crossover in systems with a liquid–liquid phase transition. *PNAS*, 102:16558–16562, 2005.

Q. Zheng, D. J. Durben, G. H. Wolf, and C. A. Angell. Liquids at Large Negative Pressures: Water at the Homogeneous Nucleation Limit. *Science*, 254(5033):829–832, Nov. 1991.