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# Speed of sound measurements in supercooled water at temperatures between (254.65 and 273.15) K and at pressures up to 190 MPa

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ABSTRACT

Experimental speed of sound measurements in supercooled ordinary water (freshly double-distilled) at temperatures between (254.65 and 273.15) K and for pressures up to 190 MPa were performed and reported. During the measurements cycles, some pre-freezing processes and phase transitions in the water were observed and reported as a contribution to further investigations for understanding of the process at a molecular level.

Our 35 speed of sound results for the liquid state metastable with respect to Ice Ih are the first such results measured with the double *pulse-echo* technique. The estimated relative expanded uncertainty ($k = 2$) is better than 0.02% for pressures up to 10 MPa and better than 0.05% in the higher pressure range.

The obtained speed of sound data have been compared, in stable states, with values predicted by the reference equation for pure water (IAPWS-95 formulation) of Wagner and Pruß and, in metastable state, with those calculated from the Equation of state (EoS) for supercooled water by Holten et al. All relative deviations are within the uncertainties stated for the equations. The comparison of the obtained results with the most recent speed of sound data by Lin and Trusler and by El Hawary and Meier shows that all the results are consistent and the agreement is within the declared uncertainties.

## 1. Introduction

Accurate knowledge of the thermophysical properties of water finds direct applications in many scientific fields, ranging from the physics of the atmosphere and meteorology, chemical physics, metrological applications, medicine and biology (preservation of cell, organs and proteins) and also for the design of food processing (deep freezing process). Even if the properties of water have been deeply investigated for stable states, for metastable states the number of available measurements is unsatisfactory.

Metastable are the states of the matter which “should not be there”, but which still can be observed, even if only not for a long time. Water, for example, if is cooled below its normal freezing temperature, is called supercooled water. It can remain liquid, but just for a limited time, and it then solidify abruptly. Metastable states are not equilibrium states. Physically, these states are reached starting from equilibrium states and by slowly changing the thermodynamic state, such as the temperature (or magnetic field). Metastable states play some important and key roles in many fields, for instance, in gas lasers: in a number of gas lasers, helium atoms are excited into metastable states by an electrical discharge. Considering the particular metastable state of the supercooled water, some of the main applications are in the field of the refrigeration for organ preservation. In this case, for example, livers that were later transplanted into recipient animals were preserved by supercooling at the temperature of -6 °C for up to 4 days, quadrupling the limits of what could be achieved by conventional liver preservation methods [1].

Today, the most accurate and thermodynamically coherent formulation for the properties of water, both in liquid and vapour phase, including metastable states, is that of Wagner and Pruß [2], known as IAPWS-95, which is the standard of the International Association for the Properties of Water and Steam (IAPWS).

IAPWS is currently reviewing the IAPWS-95 formulation, with the long term goal of removing some minor unphysical behaviours and to improve the accuracy of the predictions of the thermodynamic properties in both stable and metastable states.

All existing measurements were carefully considered in developing IAPWS-95 formulation, which is valid for the stable fluid phase. However, IAPWS considers desirable to develop a formulation with an extended range of validity that includes the supercooled liquid where extrapolations of IAPWS-95 are unsatisfactory. The IAPWS-95 formula-

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tion, for temperatures in the range of 253 K to 303 K, and pressures up to 400 MPa, shows unexpectedly large deviations from experimental speed of sound data that have been published after IAPWS-95 was developed.

Usually, the uncertainty of measurements collected in metastable states are larger than those obtained in stable states, because adopted sensors must be able to support sudden changes during phase transitions. The case of freezing water is particularly critical since, for pressures up to 210 MPa, the ice expands, generating significant mechanical stresses on the measurement cells and sensors.

For speed of sound measurements, $w$, the availability of experimental measurements in metastable states are, mainly, limited to atmospheric pressure [3–6]. Few other publications are available, but the uncertainty of the results is not reported or cannot be estimated, for example as reported in [7]. For states above atmospheric pressure, there are only a few accurate sound-speed measurements in metastable states reported within papers focused on stable states [8–13].

For measurements at high pressure, only a few results are available for speed of sound in supercooled water. For example, in the case of Vance and Brown [10] results are affected by an uncertainty in the range of (0.2 – 0.3) % or the values obtained by Lin and Trusler [12] with a relative uncertainty ranging from 0.02% to 0.03%. Considering also the measurements of Petitet et al. [8], $u_r(w) = 0.1\%$, and Hidalgo Balsar et al. [11], $u_r(w) < 0.2\%$, the number of available values is of approximately ten, which is not sufficient to extend the IAPWS formulation to metastable states. For these reasons, it has been decided to start a systematic investigation of the speed of sound mainly focused on metastable states of water.

Based on the measurements available in 2014, Holten et al. [14] published a fundamental equation dedicated to describe metastable states, for temperature up to 300 K and for pressures up to 400 MPa. That formulation declared, for the speed of sound predictions, a relative uncertainty of 0.5% for temperatures above 254.15 K and for pressures below 190 MPa, while for stable states the relative uncertainty was estimated to be 0.1%. Above 273.15 K, the predictions have an uncertainty ranging from 0.02% to 0.05%. Remarkably, the formulation of Holten et al. performs better than expected by its authors, when it is compared with the new experimental results reported here.

## 2. Speed of sound measurement method

Speed of sound has been measured using the double *pulse-echo* method that makes use of a single source of ultrasonic tone bursts, composed by 5 cycles each, at a carrier frequency of 4 MHz. The source is made of a piezoelectric disc with a diameter of 7 mm excited in thickness-mode. The generated waves are emitted on a single line and in opposite directions. Two reflectors are set at a nominal distance of $L_1 = 45$ mm and $L_2 = 67.5$ mm, so that signals are reflected back to the source at different times. Having travelled different distances at the same speed, ultrasonic waves appear separated on the digital oscilloscope. The waveforms of the two tone bursts are sampled and then correlated to determine the time delay, $\tau$, separating them from. In this framework, the speed of sound can be calculated as:

$$w = \frac{2(L_2 - L_1)}{\tau} = \frac{2\Delta L}{\tau} \,, \tag{1}$$

where $2\Delta L$ is a function of the temperature and pressure since the stainless steel, which the cell is made of, has its own thermal expansion coefficient and isothermal compressibility. A complete description of the measurement principle, corrections and limitations can be found in [15] and [16].

## 3. Experimental section

The measurements of the thermodynamic properties of fluids in equilibrated metastable conditions raise difficulties usually not faced when carried out in stable states. In fact, since a system can remain in a metastable state only for limited time, the apparatus has to withstand the energy release when the transition to a stable state occurs. In the case of freezing water, for pressure below approximately 210 MPa, it has to be expected that the ice expands, generating a sudden increase of pressure. Depending on the volume of the pressure vessel, the pressure can increase by as much as 100 MPa, generating an extra stress on the mechanical parts of the experimental apparatus, in particular, for the case of *pulse-echo* technique, on the measurement cell and on the pressure transducer. For this reason, it was decided to prefer a robust pressure gauge to a very accurate sensor and a kapton-encapsulated piezoceramic ultrasonic source to the traditional metallized piezoceramic disk.

The temperature control system is made of two stages. Usually, the first stage is used to reach a temperature that is few hundredths of a kelvin below the measurement set-point, then the second stage leads the temperature to the set-point only by heating the fluid. However, if measurements are performed in metastable conditions, the first stage must be accurately controlled when the phase-transition line is crossed.

Sometimes, although the cooling speed of the first stage thermostat was so low that either the second stage was not necessary, the transition occurred before a stable speed of sound was reached, so that a measurement could not be performed. In those cases, it was decided to fix the temperature of the system and cross the phase-transition line by changing the pressure. During this operation, the temperature is only slightly perturbed and the measurement can be performed when the obtained values of speed of sound are stable. For changes in temperature, the cooling speed was usually set to 0.3 K/h; this method was mainly used for collecting measurements above 264.15 K. Conversely, at lower temperature, it was preferred to reduce the pressure at a rate of 0.2 MPa/s.

To reach the measurement point, whatever the thermodynamic path was, the first thermodynamic points of a new data set were measured in compressed liquid. This approach was chosen to verify the apparatus performance before beginning a new cycle or when the system had frozen in the previous measurement cycle. Comparing the stable states measurements with those predicted by the IAPWS-95 formulation [2] or those of Lin and Trusler [12] allowed us to verify that both the calibration of both the pressure gauge and the speed of sound cell were preserved after every mechanical shock. The amplitude and the shape of each ultrasonic signal were qualitatively compared to those of the previous cycles to monitor the status of the ultrasonic source. Despite different transition events, the adopted encapsulated piezoelectric source was not damaged and its performance did not show any degradation, when compared with the calibration measurements performed before the measurements cycles.

### 3.1. Freezing process

When the fluid is in a metastable state, it can rush to a stable state in an uncontrolled way. During the measurement cycles, it was possible to monitor some of those processes. As an example, Fig. 1 shows the measured pressure (a) as a function of the time and the corresponding temperature (b). Water was in a metastable liquid at $t = 0$ min and the cooling process went on for 10 min when freezing occurred. The freezing process took at least 20 s to start and took approximately 7 min to complete. The solid-liquid equilibrium was reached at the pressure of 127.81 MPa, and this value has been used to calculate the temperature of transition of 261.19 K, the horizontal line in Fig. 1(b), using the IAPWS formulation for the melting pressure [17]. The temperature of transition measured by our thermometers was 261.195 K, and thus the agreement is well within the uncertainty of the temperature sensor (0.01 K). It is also to be considered that thermometers were set in the thick walls of the pressure vessel and that the temperature of the thermostat was not set at the transition temperature, so that residual heat fluxes have actually perturbed the measurement of the temperature. At minute 40, the melting procedure was started by increasing the temperature of the thermostat and the consequent reduction of the pressure

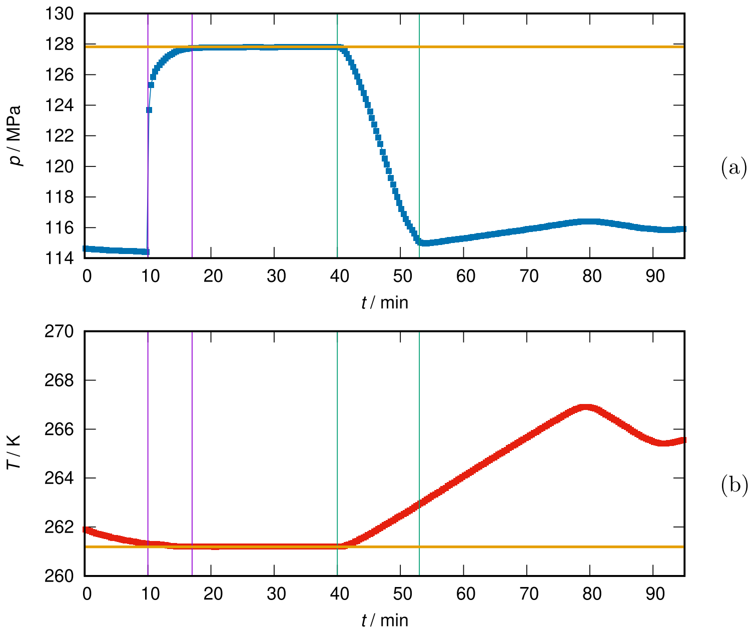

**Fig. 1.** Freezing process of water from a metastable state. The pressure and the temperature have been measured as a function of the time and reported in plot (a) and (b) respectively.

was observed. When water was frozen, ultrasonic signals were very attenuated and it was decided to suspend the measurement of speed of sound.

During the first measurement cycles, it was difficult to predict when water was about to freeze and transitions occurred unexpectedly. That situation was frustrating because re-melting the sample, heating, checking the system and restarting the measurement required a long time. However, after some tests, it became clear that there were small repeatable oscillations of amplitude of the ultrasonic signals and of the pressure, not affecting the speed of sound measurements, that were recognizable up to an hour before the freezing event. If these behaviours appeared when temperature and pressure conditions were close to the melting line, then it was possible to restore the system to a stable condition before freezing occurred.

In supercooled water there are always fluctuations in structure which give rise to rapid microscopic variations in quantities such as density, temperature and pressure [18]. During the measurements cycles, it was possible to observe the formation and dissolution of clusters when the system was kept in metastable states for long time, usually for temperature and pressure close to the melting line. For example, when the system was set at 262.15 K and 100 MPa for hours, suddenly, the pressure started to slowly increase. The pressure was recorded and the plot in Fig. 2 shows the variations with respect to the time scale. Unfortunately, it was not possible to measure the temperature. However, a preliminary and raw estimation of the dimension of total volume of the ice clusters can be done considering the partial freezing as an isochoric process at constant temperature. In this very simplified approach, the variation of the volume of the liquid per megapascal can be estimated by the expression:

$$\Delta V/\Delta p = -[nV/(n - V\Delta\rho_{\mathrm{m}})]/p, \tag{2}$$

where $n$ (≈ 7 mol) is the number of moles of water sealed into the pressure vessel at 262.15 K and 110 MPa, $V$ ($\approx 120\times10^{-}6\ \mathrm{m}^3$) is the volume of liquid injected in the vessel, including tubes till the first closed valve, $\Delta\rho_{\mathrm{m}}$ ($\approx 20\ \mathrm{mol/m}^3$) is the variation of the molar density of the liquid water when the pressure $p = 110$ MPa changes by 1 MPa. In this approximation, the variation of the liquid volume was estimated in $\Delta V/\Delta p = -1.2\ \mathrm{cm}^3/\mathrm{MPa}$, that is occupied by ice of type Ih. At the end of the process, the pressures reached 114 MPa and the sample was in liquid phase because the acoustic signal was visible. This mean that, probably, the temperature of the water increased by about 1 K. In this view, the size of the clusters is probably a bit overestimated, however, it allows to better figure out the process described in Fig. 2. This effect should be further investigated, since it could play an important role for food industries and for preserving biological tissues.

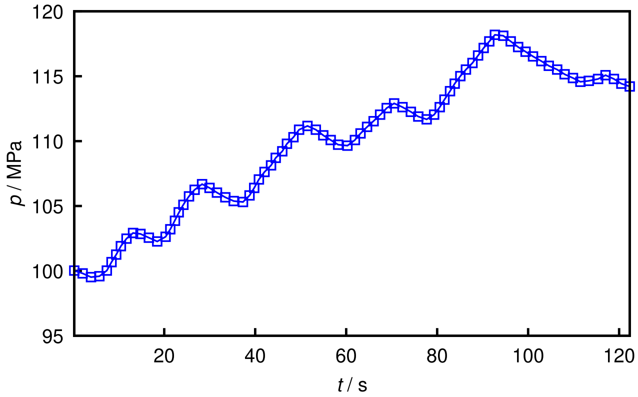

**Fig. 2.** Formation and dissolution of ice-clusters in metastable states.

### 3.2. Experimental apparatus

The experimental apparatus, developed at INRiM for measuring speed of sound in liquids, implements a double reflector *pulse-echo* technique. The main features of the apparatus design (with regard to the choice of dimensions, constructing materials, gaskets, etc...) make it a versatile instrument able to operate with a wide range of fluids of significantly different thermodynamic properties, over wide intervals of temperatures and pressures. The measurement procedure was aided by a computer and partially automatized by a control program. A diagram of the ultrasonic cell is shown in Fig. 3. It was made of a AISI 316L stainless steel, in which the ultrasonic piezoelectric transducer (a wide-band ceramic PZT “Dura Act” kapton encapsulated), is clamped at its edge by two conical stainless steel supports, that reduce the effective radius from 10 mm to about 7 mm, without changing the thickness of the disc. The conical shape surrounded the source minimized the interfering effect of

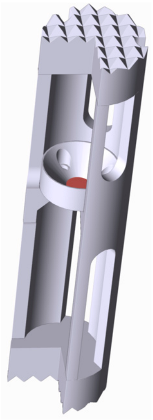

**Fig. 3.** Diagram of the ultrasonic cell implementing the double *pulse-echo* measurement method. The piezoelectric disk is visible in red color.

diverging components of the acoustic beam which may be reflected on the transducer. The cone was fixed to the cell by means of three screws. Two solid stainless steel reflectors (of about 15 mm of thickness), having plane smooth surfaces, were fixed to the ends of the cell spacers. The outer surfaces of the reflectors were cut with a series of pyramid-shaped incisions, in order to maximize dispersion of sound passing through the reflectors, thus avoiding back-reflection into the cell.

The ultrasonic cell can operate in the temperature range between (180 and 470) K and for pressures up to 400 MPa, when set in the pressure vessel sealed with AISI-316L metallic gaskets. Fig. 4 shows a diagram of the measurement apparatus, where the high-pressure system consists of three main sections: the pressure vessel (reported on the right in the figure), a pressure transducer, directly connected to the vessel, and a pressure control hydraulic circuit including a pressure amplifier. The vessel and the pressure transducer can be completely isolated from the other parts of the control system in order to minimize heat exchange between the thermostatted vessel and the ambient environment. The pressure vessel, specifically designed for this application, was made of a stainless steel alloy and has an internal volume of 120 cm$^3$ (when cell is inside). It was provided with a coaxial pressure-tight electrical feed-through for high frequency signals transmission to the inside ultrasonic cell and can be operated at pressures up to 300 MPa. The temperature of the sample was measured by means of two PT100 thermometers inserted in the top and the bottom stoppers of the pressure vessel. These thermometers were calibrated in the range of (230 and 390) K by comparison with INRiM's (Istituto Nazionale di Ricerca Metrologica) Standard Platinum Resistance Thermometer (sPRT) directly traceable to the National Temperature Standard. A liquid bath thermostat (Kambic Calibration Bath mod. OB-25/2 ULT) maintains the temperature of experiment with a long term stability better than ±1 mK at ambient temperature and of ±5 mK between (220 and 285) K. The pressure is measured by three industrial Honeywell TJE pressure transducers with different full scale that can be isolated one by one, when the pressure approaches the measurement limit.

### 3.3. Preparation of the apparatus

Experimental apparatus was loaded using a sample of pure water obtained using a stainless steel double distiller. The sample density was measured using a hydrostatic weighing densimeter with an expanded relative uncertainty of 12 parts per million ($k = 2$) and the obtained value agrees with that predicted by the IAPWS-95 formulation within 3 parts per million. Table 1 briefly reports the characteristics of the adopted water sample. Considering the expected uncertainty associated

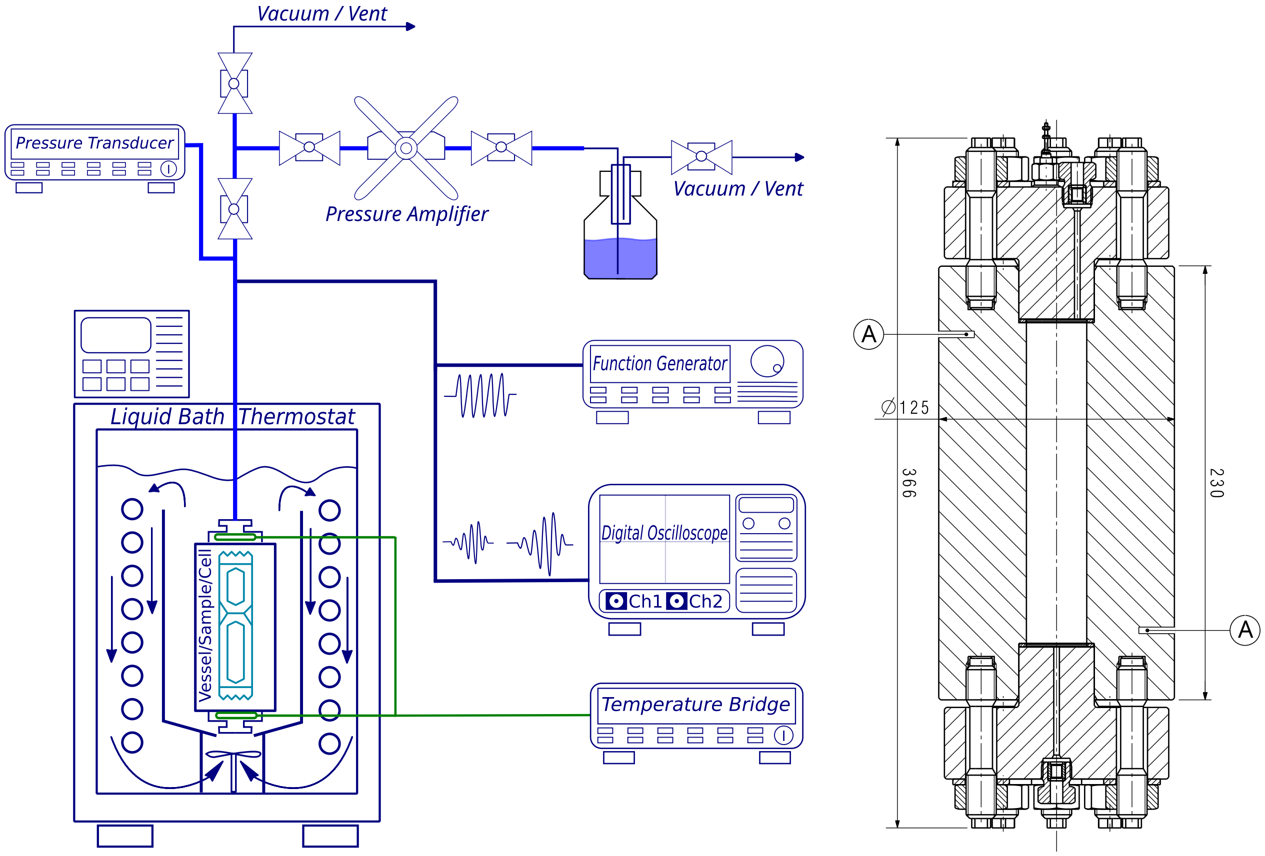

**Fig. 4.** On the left: the diagram of the experimental system. On the right: the draw of the section of the pressure vessel, where the circled "A" letters indicate the position of the thermometers.

**Table 1**
Specification of the used sample obtained using a stainless steel double distiller.

| | | | |
|---|---|---|---|
| **Sample name:** | Water | **Molecular Formula:** | $H_2O$ |
| **Density at 20 °C:** | (998.192 ± 0.012) kg/m$^3$ at 20.086 °C and 998 mbar | **Conductivity:** | (1.4 ± 0.1) μS at 25 °C |
| **Appearance (color):** | colourless | **Appearance (form):** | Liquid |
| **Particles (d < 0.22 μm):** | c < 1 (1/ml) | **Sample volume:** | 250 ml at 20 °C |

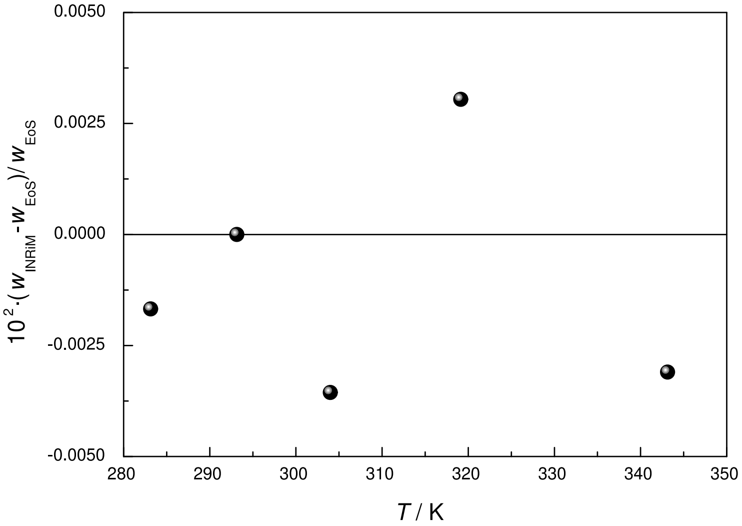

**Fig. 5.** Results of the calibration of the speed of sound sensor in ordinary water at 0.098 MPa and at different temperatures. Relative deviations of experimental speeds of sound $w_{\text{INRiM}}$ from values $w_{\text{EoS}}$ calculated with the EoS of Wagner and Pruß are plotted as a function of the temperature.

with speed of sound measurements, the isotopic composition of the sample has negligible effects compared to other sources of uncertainty.

As a preliminary procedure, the entire high pressure manifold was rinsed with pure bi-distilled water and subsequently drained and dried by a flow of compressed nitrogen. The system was then evacuated for 12 h, by a mechanical vacuum pump, with a liquid nitrogen trap, to eliminate any residual trace of water and/or air. To prevent the contamination of the sample and the influence of dissolved gases, the high pressure manifold and the ultrasonic cell were filled, under vacuum, by the extraction of pure degassed water from an ambient pressure reservoir.

Considering the effects of transition from metastable liquid to solid, the most stressed sensor is the pressure transducer. For this reason, three capacitive transducers, with full-scale of 10 MPa, 200 MPa and 400 MPa, were calibrated before and after each measurement cycle. Calibrations showed that, despite some pressure shocks occurring during measurement cycles, the transducers have been subjected to a small drift of 0.02 MPa and 0.04 MPa, respectively, for the 200 MPa and 400 MPa sensors. Calibration drift was maintained within a tenth of the declared uncertainty of the transducers, so it was decided not to apply further corrections.

The acoustic path length was calibrated by comparing the obtained speed of sound measurements in high-purity ordinary water at five different temperatures (283.15, 293.15, 304.0, 319.15, 343.15) K, in liquid phase and at 0.098 MPa, with reference speed of sound values from the IAPWS-95 formulation. The relative deviations of our experimental results ($w_{\text{INRiM}}$) from the speed of sound values calculated ($w_{\text{EoS}}$) with the equation of state by Wagner and Pruß [2] are plotted as a function of temperature in Fig. 5. The relative uncertainty declared by Wagner and Pruß in the considered region is 0.005%, and all our results are in good agreement with those obtained by the reference equation of state. Furthermore, after that, in order to check the cell stability at high pressure also, it was chosen to make a second calibration at higher pressure (20.003, 60.002, 100.010) MPa and at the temperature of 295.45 K (see Fig. 6). After the first freezing, the calibration was repeated also at 288.15 K and 150 MPa.

In view of the expected uncertainty of the experimental results, the choice of using more accurate reference values, from specific publications, would have not provided significantly better results. The obtained cell calibration was verified whenever the speed of sound was measured in the stable liquid region. In this way, it was possible to ensure that mechanical shocks didn't deteriorate the cell performance cycle by cycle.

Additional experimental tests were carried out to verify that the calibrated length did not vary as the carrier frequency of the signal was changed. Three different runs have been performed using tone-burst of 5 cycles with a carrier frequency of 4 MHz, three runs with a carrier frequency of 5 MHz and three additional runs at 8 MHz. The results showed that the frequency dependence of the time-of-flight was negligible ( < 40 ppm), when compared to other sources of uncertainty so that, the speed of sound measurements were performed at 5 MHz. To minimize the effect of temperature drifts in the order of a few millikelvins, the calibration has been repeated three times and the results have been averaged. These tests were carried out at ambient pressure and at the temperature of 293.15 K.

### 3.4. *Measurement procedure*

The experimental apparatus was designed so that both the temperature and the pressure of the pressure vessel can be controlled by changing the set-point of the thermostat and/or by acting on the pressure amplifier respectively.

Speed of sound has been measured in the temperature range of 264.65 K to 273.15 K and for pressures up to 190 MPa. The explored region overlaps the region where ice Ih is stable; further investigations will be extended to the region where liquid is metastable with respect to ice III. Fig. 7 shows the investigated points, in terms of temperature and pressure, and the melting line for water.

The first measurements were started in the compressed liquid $T - p$ region at 273.15 K and 150 MPa and were collected down to 5 MPa, with variable steps of pressure, for checking that the measurement cell was working correctly.

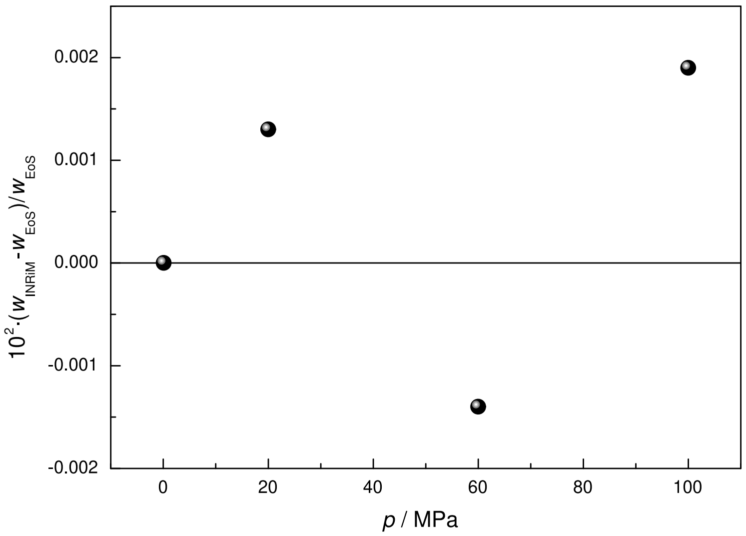

**Fig. 6.** Results of the calibration of the speed of sound sensor in ordinary water at 295.5 K and at different pressures. Relative deviations of experimental speeds of sound $w_{\mathrm{INRiM}}$ from values $w_{\mathrm{EoS}}$ calculated with the EoS of Wagner and Pruß are plotted as a function of the pressure.

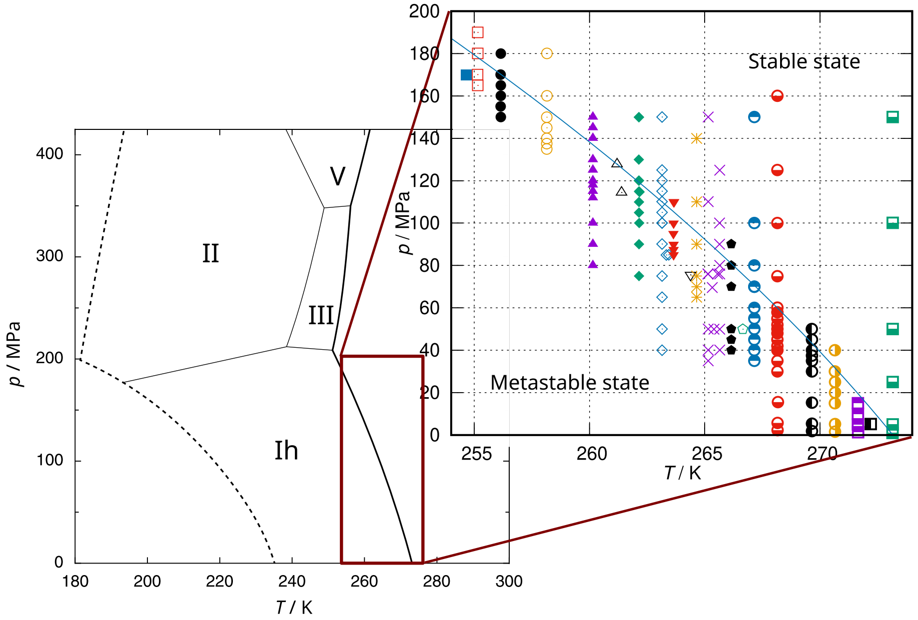

**Fig. 7.** Experimental temperature and pressure conditions where speed of sound was measured. Symbols denote (■) 254.65 K, (□) 255.15 K, (●) 256.15 K, (○) 258.15 K, (▲) 260.15 K, (△) 261.20 K and 261.39 K, (◆) 262.15 K, (◇) from 263.14 K to 263.440 K, (▼) 263.65 K, (▽) 264.38 K, (✳) 264.65 K, (×) from 265.14 K to 265.65 K, (⬟) 266.15 K, (⬠) 266.65 K, (◓) 267.15 K, (◒) 268.15 K, (◐) 269.65 K, (◑) 270.65 K, (⬒) 271.65 K, (◧) 272.20 K, (⬓) 273.15 K; while the melting conditions are represented by the solid line.

For the measurements performed in metastable conditions, two different approaches were used: changing the temperature or the pressure.

At first, around 270 K, it was decided to change the temperature and consequently a pressure variation was obtained. In particular, reducing the temperature at 271.65 K, the pressure found its new equilibrium at 1.32 MPa. In the next step, temperature was reduced by 1.0 K and the corresponding pressure became 1.56 MPa, and so on until the system froze at the temperature 266.15 K, unfortunately before being able to perform the measurement. The ice was melted at 273.15 K and 5 MPa to restart the measurements. Then, with the aim of understanding the behaviour of the system during temperature and pressure changes in metastable states, the temperature was decreased to 272.15 K at a speed of 0.3 K/h. Accordingly, the pressure increased to 5.13 MPa. This effect is known as one of the anomalies of water that shows a maximum density at 277 K at atmospheric pressure. This local maximum is shifted at lower temperatures when the pressure is increased.

In a second moment, since for some slow temperature descents, when measurement conditions were more than 5 K below the melting line, the system froze before being able to reach the necessary equilibrium for recording the speed of sound value, it was chosen to fix the temperature and reduce the pressure, starting from a stable state.

So, for the isotherms at 266.15 K, 264.65 K, 258.15 K and few others isotherms it was chosen to cross the melting line by reducing the pressure and the temperature followed. In particular, for temperatures above 264.15 K, the rate of the pressure variations was of 10 kPa/s, but at that rate the system froze just a few megapascal below the melting line. For temperatures below 264.15 K, the rate of pressure variation was increased to 200 kPa/s. By this method, it was possible to investigate deeper metastable states. Better results were obtained when pressure

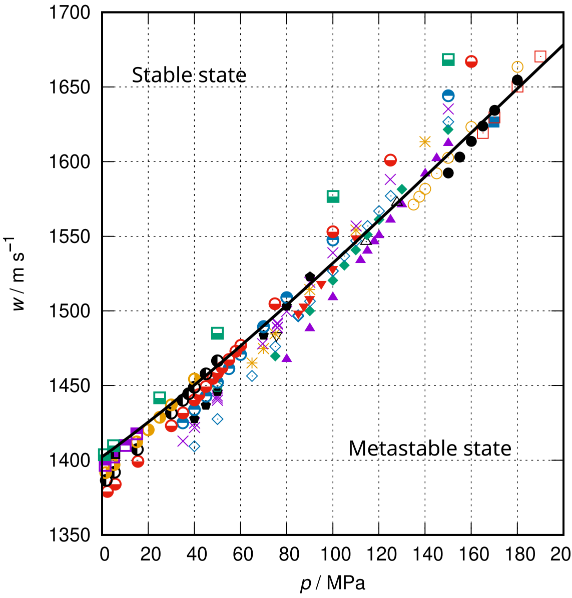

**Fig. 8.** Experimental speed of sound results as a function of the pressure. Symbols belong to (■) 254.65 K, (□) 255.15 K, (●) 256.15 K, (○) 258.15 K, (▲) 260.15 K, (△) 261.20 K and 261.39 K, (◆) 262.15 K, (◇) from 263.14 K to 263.440 K, (▼) 263.65 K, (▽) 264.38 K, (✳) 264.65 K, (×) from 265.14 K to 265.65 K, (⬟) 266.15 K, (⬠) 266.65 K, (◓) 267.15 K, (◒) 268.15 K, (◐) 269.65 K, (◑) 270.65 K, (⬒) 271.65 K, (◧) 272.20 K, (⬓) 273.15 K; while the melting conditions are represented by the solid line.

was deceased at a relatively high rate (≈ 0.5 MPa/s). Even better results were obtained when pressure descents of 10 MPa were separated by 5 minute pauses. After experimenting with different ways of failure, the introduction of the stops allowed reaching the lowest pressure, maintaining the sample in the liquid state.

Since metastable states are destined to precipitate to a stable solid state, measurements were collected when they were stable for a time in the range of 5-10 minutes. Usually, we waited more than 15 minutes before recording values in a stable state. To be sure that the adopted procedure has not perturbed the accuracy of the results, some measurements were repeated after a number of cycles were concluded and some freezing events had occurred. However, the differences of the speed of sound values at the repeated thermodynamic state are within the declared uncertainty. In Fig. 8, the speed of sound values are shown as a function of pressure. The solid line of the plot represents the values of the speed of sound in the liquid phase on the melting line. Measurements below the solid line are obtained in metastable conditions.

For the measurements started at 273.15 K and 5 MPa, it was observed that, decreasing the temperature, the corresponding pressure increases; while the behaviour of the pressure was the opposite at 263.15 K and 115 MPa. This trend was also well reproduced by Holten et al. [14] in the formulation for subcooled water.

## 4. Uncertainty budget and speed of sound results

The uncertainty associated with the obtained results is calculated by combining the uncertainty contributions of the measurements of temperature $u(T)$, pressure $u(p)$, the calibrated length of the acoustic path $u(2\Delta L)$, the measured time of flight $u(\tau)$, and the repeatability $R$. Since each of the cited quantities contribute with a different sensitivity to the speed of sound uncertainty, the adopted expression is hereafter reported:

$$u_r^2(w) = \left(\frac{u(2\Delta L)}{2\Delta L}\right)^2 + \left(\frac{u(\tau)}{\tau}\right)^2 + \left(\frac{\partial w}{\partial T}\frac{u(T)}{w}\right)^2 + \left(\frac{\partial w}{\partial p}\frac{u(p)}{w}\right)^2 + R^2 , \tag{3}$$

**Table 2**
Uncertainty contributions associated to the experimental speed of sound measurements. Values are reported as standard uncertainty and the contributions are calculated including sensitivity coefficients.

| Contribution | Relative uncertainty ($p \leq 10$ MPa) | Relative uncertainty (10 MPa $< p <$ 270 MPa) |
|---|---|---|
| Acoustic path length | 0.005% | 0.0055% |
| Time of flight | 0.001% | 0.0010% |
| Temperature | 0.004% | 0.0038% |
| Pressure | 0.002% | 0.0232% |
| Repeatability | 0.002% | 0.0020% |
| Combined expanded relative uncertainty ($k = 2$) | < 0.02% | < 0.05% |

where $u_r(w)$ is the standard combined relative uncertainty of speed of sound. When measurements are performed in stable states, the repeatability usually gives only a negligible contribution. Conversely, in this case, the experimental apparatus is stressed mechanically every time that water freezes. For this reason, though it is small, the repeatability contribution cannot be neglected.

The uncertainty budget is here reported briefly, however a complete description of the adopted uncertainty models can be found in [15] and [16]. While we expected degradation of the cell's performance after each solidification, the good repeatability of the measurements obtained in both stable and metastable states proved the stability of the cell, and particularly of the pressure measurements.

Moreover, the authors have not observed neither a degradation of the amplitude of the emitted signal nor a degradation of the kapton encapsulation and the final check of the source was done dismounting the ultrasonic sensor and checking optically it at the end of the measurement cycles.

Since the evaluated uncertainty was different in different pressure ranges, it was decided to split the set of results into two classes. For pressures below 10 MPa, the expanded relative uncertainty of speed of sound measurements was evaluated to be less than 0.02% ($k = 2$); while at higher pressures it was 0.05% ($k = 2$). Table 2 reports the main sources of uncertainty and their contributions. It is worth noting that, for the lowest pressures, the uncertainty is comparable with that coming from the calibration procedure of the cell; while for measurements at the highest pressure, the uncertainty budget is dominated by the accuracy of the measurement of the pressure. That behaviour is typical of the adopted capacitive pressure transducers and it was not attributable to the metastable conditions of the sample.

Obtained experimental speed of sound measurements are reported in Table 3 where the values in bold font indicate repeated measurements, reproduced after some freezing events, performed to check the stability of the experimental apparatus. Since differences are maintained well within the declared uncertainty, the measurement system was shown to preserve its performance.

## 5. Comparison with equation of state predictions

As a further check of the performance of the measurement cell, some of the points measured by Lin and Trusler [12] at 263.28 K and at 273.21 K were reproduced. In this case, our speed of sound values were fitted by a polynomial function of the fourth degree in pressure and of the second order in temperature, so that fit residues were less than half of the calculated uncertainty values.

For both the considered isotherms, speed of sound results differed by no more than 0.03%, which is also the uncertainty declared by Lin and Trusler. Deviations showed a weak pressure dependence for the isotherm at 273.21 K, however this effect was not observed when measurements are compared with those of El Hawary and Meier [13], for the isotherm at 273.64 K. In this case, the agreement was within our combined uncertainty, considering that El Hawary and Meier declared

**Table 3**

Experimental speed of sound values in supercooled water as a function of the temperature and pressure. The expanded relative uncertainty of the reported results is $U_r(w) = 0.02\%$ ($k = 2$) for $p < 10$ MPa and $U_r = 0.05\%$ ($k = 2$) for $p > 10$ MPa. The uncertainty of the temperature and pressure measurements are 0.01 K and 0.2 MPa (0.001 MPa for $p < 10$ MPa), respectively. Values reported in italic correspond to measurements in metastable states, while repeated measurements are reported in bold.

| $T$/K | $p$/MPa | $w$/(m/s) |
|---|---|---|
| *254.649* | *169.78* | *1626.66* |
| *255.153* | *165.02* | *1619.14* |
| *255.149* | *170.04* | *1629.56* |
| 255.153 | 180.07 | 1650.29 |
| 255.150 | 190.00 | 1670.42 |
| *256.150* | *150.03* | *1592.42* |
| *256.150* | *155.03* | *1602.98* |
| *256.151* | *160.05* | *1613.54* |
| *256.153* | *165.01* | *1623.87* |
| *256.149* | *170.12* | *1634.39* |
| 256.151 | 180.01 | 1654.65 |
| *258.148* | *135.01* | *1571.20* |
| *258.148* | *137.53* | *1576.50* |
| *258.149* | *140.02* | *1581.69* |
| *258.149* | *145.01* | *1592.12* |
| *258.149* | *150.00* | *1602.47* |
| 258.153 | 160.07 | 1623.24 |
| 258.151 | 180.04 | 1663.51 |
| *260.151* | *80.02* | *1467.56* |
| *260.152* | *90.00* | *1488.21* |
| *260.151* | *100.03* | *1509.06* |
| *260.150* | *112.00* | *1533.89* |
| *260.150* | *115.01* | *1540.16* |
| *260.151* | *118.01* | *1546.43* |
| *260.150* | *120.02* | *1550.60* |
| *260.150* | *125.02* | *1560.97* |
| *260.150* | *130.01* | *1571.30* |
| 260.151 | 140.03 | 1591.94 |
| 260.152 | 145.05 | 1602.19 |
| 260.148 | 150.03 | 1612.31 |
| *261.196* | *127.81* | *1572.57* |
| *261.390* | *114.44* | *1546.39* |
| 262.175 | 114.71 | 1551.040 |
| *262.149* | *75.06* | *1469.76* |
| *262.148* | *90.05* | *1500.05* |
| *262.154* | *100.02* | *1520.46* |
| *262.150* | *104.99* | *1530.59* |
| *262.150* | *110.00* | *1540.82* |
| *262.150* | *115.00* | *1551.04* |
| **262.140** | **120.02** | **1561.22** |
| **262.150** | **120.05** | **1561.28** |
| 262.144 | 129.99 | 1581.47 |
| **262.144** | **149.99** | **1621.48** |
| **262.148** | **150.00** | **1621.51** |
| *263.148* | *40.03* | *1409.42* |
| *263.148* | *49.99* | *1427.65* |
| *263.150* | *65.01* | *1456.47* |
| *263.149* | *75.03* | *1476.26* |
| *263.147* | *90.10* | *1506.43* |
| ***263.148*** | ***100.02*** | ***1526.70*** |
| ***263.145*** | ***100.00*** | ***1526.67*** |
| *263.151* | 105.01 | 1536.77 |
| *263.151* | *110.09* | *1547.03* |
| *263.150* | *115.05* | *1556.89* |
| 263.147 | 120.02 | 1566.86 |
| 263.150 | 125.06 | 1576.99 |
| 263.149 | 150.08 | 1626.67 |
| *263.330* | *84.99* | *1496.38* |
| *263.440* | *84.99* | *1497.06* |
| *263.645* | *85.08* | *1498.36* |
| *263.645* | *87.48* | *1503.18* |
| *263.645* | *89.98* | *1508.17* |
| *263.644* | *95.00* | *1518.21* |
| *263.647* | *99.99* | *1528.26* |
| **263.652** | **110.08** | **1548.61** |
| **263.677** | **110.09** | **1548.76** |
| *264.379* | *75.56* | *1483.71* |
| *264.650* | *65.00* | *1465.23* |
| *264.650* | *69.95* | *1474.83* |
| *264.652* | *74.99* | *1484.64* |
| *264.651* | *90.01* | *1514.27* |
| 264.653 | 110.08 | 1554.20 |
| 264.651 | 140.01 | 1613.36 |
| *265.148* | *35.05* | *1412.90* |
| *265.150* | *40.12* | *1421.94* |
| *265.152* | *49.99* | *1440.22* |
| ***265.143*** | ***75.99*** | ***1488.92*** |
| ***265.143*** | ***75.99*** | ***1488.94*** |
| 265.150 | 110.14 | 1556.90 |
| 265.149 | 150.04 | 1635.21 |
| *265.325* | *69.60* | *1478.03* |
| *265.399* | *49.94* | *1441.65* |
| *265.557* | *75.99* | *1491.27* |
| *265.650* | *40.07* | *1424.91* |
| *265.652* | *49.93* | *1443.15* |
| *265.651* | *76.01* | *1491.81* |
| *265.650* | *80.01* | *1499.62* |
| 265.645 | 90.01 | 1519.22 |
| 265.644 | 100.04 | 1538.97 |
| 265.651 | 124.95 | 1588.08 |
| *266.151* | *40.01* | *1427.86* |
| *266.153* | *44.99* | *1436.86* |
| *266.150* | *50.04* | *1446.08* |
| *266.150* | *70.01* | *1483.80* |
| *266.150* | *80.06* | *1503.25* |
| 266.149 | 90.09 | 1522.850 |
| *266.653* | *49.94* | *1449.13* |
| *267.151* | *35.01* | *1424.98* |
| *267.150* | *40.02* | *1433.83* |
| *267.150* | *45.03* | *1442.84* |
| *267.153* | *50.01* | *1452.17* |
| *267.151* | *60.06* | *1470.82* |
| ***267.149*** | ***70.01*** | ***1489.60*** |
| ***267.151*** | ***69.95*** | ***1489.32*** |
| 267.149 | 80.05 | 1508.84 |
| 267.148 | 100.02 | 1547.53 |
| 267.149 | 150.04 | 1644.12 |
| *268.155* | *2.30* | *1379.08* |
| *268.156* | *5.72* | *1384.04* |
| *268.172* | *15.54* | *1399.21* |
| *268.151* | *30.02* | *1423.10* |
| *268.149* | *35.02* | *1431.71* |
| *268.150* | *40.00* | *1440.45* |
| *268.150* | *42.02* | *1444.05* |
| *268.152* | *45.00* | *1449.37* |
| *268.151* | *47.99* | *1454.77* |
| *268.150* | *50.03* | *1458.48* |
| *268.150* | *52.00* | *1462.07* |
| *268.149* | *54.94* | *1467.49* |
| *268.149* | *57.93* | *1472.99* |
| 268.150 | 60.09 | 1476.99 |
| 268.149 | 74.90 | 1504.84 |
| 268.150 | 100.01 | 1552.99 |
| 268.152 | 125.03 | 1600.99 |
| 268.149 | 160.03 | 1667.09 |
| *269.650* | *1.83* | *1386.58* |
| *269.651* | *5.37* | *1391.96* |
| *269.652* | *15.28* | *1407.24* |
| *269.650* | *30.03* | *1431.62* |
| *269.650* | *35.00* | *1440.15* |
| *269.650* | *37.51* | *1444.52* |
| *269.650* | *40.01* | *1448.90* |
| 269.649 | 45.04 | 1457.81 |
| 269.642 | 50.01 | 1466.59 |
| *270.651* | *1.56* | *1391.63* |
| *270.652* | *5.18* | *1397.12* |
| *270.645* | *15.02* | *1412.39* |
| *270.648* | *20.01* | *1420.44* |
| *270.648* | *25.00* | *1428.69* |
| *270.646* | *30.00* | *1437.10* |
| 270.647 | 40.00 | 1454.43 |
| *271.650* | *1.32* | *1396.54* |
| *271.645* | *5.00* | *1402.16* |
| *271.648* | *10.02* | *1409.88* |
| *271.645* | *15.01* | *1417.74* |
| *272.197* | *5.14* | *1405.13* |
| 273.148 | 0.99 | 1403.79 |
| 273.150 | 4.96 | 1409.76 |
| 273.150 | 24.98 | 1441.81 |
| 273.151 | 50.01 | 1485.04 |
| 273.151 | 100.10 | 1576.57 |
| 273.152 | 150.03 | 1668.27 |

a relative uncertainty of 0.007%. The results of the comparisons are reported in Fig. 9, where the excellent agreement is visible.

Unfortunately, it was not possible to compare our results with those of Taschin et al. [6], because our measurements were obtained for pressures higher than 1 MPa, in order to preserve the purity of the water sample. However, it was possible to compare the measurements with those predicted by the IAPWS-95 formulation, which is being extrapolated outside its range of validity in the metastable region, as reported in Fig. 10, and with the one produced by the formulation of Holten et al. [14], specifically developed for metastable states (liquid low temperature water), as shown in Fig. 11. The agreement with the IAPWS-95 formulation becomes worse with decreasing temperature, but it is recovered for stable liquid states. For stable states, IAPWS-95 claimed uncertainty is of 0.1%, while for metastable states no uncertainty was claimed since they are outside the range of validity of IAPWS-95.

However, since deviations grow monotonically when reducing the temperature, small corrections to the formulation might significantly improve its accuracy.

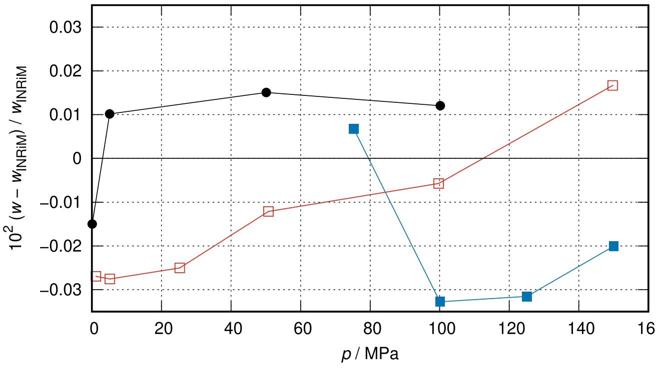

**Fig. 9.** Comparison of the obtained results with published accurate measurements obtained in the overlapping temperature and pressure ranges selected in this work: (■) Lin and Trusler [12] at 263.28 K (partially in metastable states), $U_\mathrm{r}(w) = 0.03\%$ ($k = 2$); (□) Lin and Trusler at 273.21 K (stable states), $U_\mathrm{r}(w) = 0.03\%$ ($k = 2$); (●) El Hawary and Meier [13] at 273.65 K (stable states), $U_\mathrm{r}(w) = 0.007\%$ ($k = 2$).

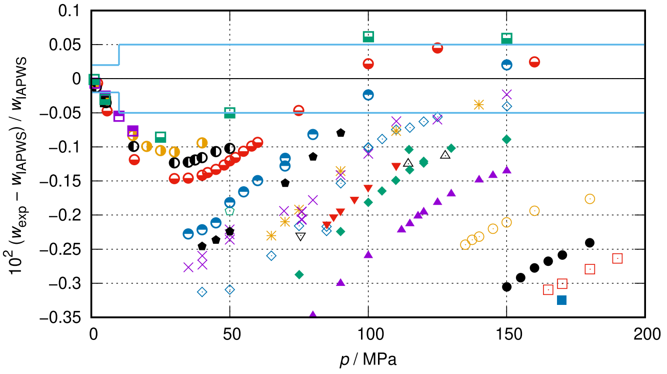

**Fig. 10.** Comparison of the experimental speed of sound measurements with those predicted by the IAPWS-95 formulation. Symbols denote (■) 254.65 K, (□) 255.15 K, (●) 256.15 K, (○) 258.15 K, (▲) 260.15 K, (△) 261.20 K and 261.39 K, (◆) 262.15 K, (◇) from 263.14 K to 263.440 K, (▼) 263.65 K, (▽) 264.38 K, (✳) 264.65 K, (×) from 265.14 K to 265.65 K, (⬟) 266.15 K, (⬠) 266.65 K, (◓) 267.15 K, (◒) 268.15 K, (◐) 269.65 K, (◑) 270.65 K, (⬒) 271.65 K, (◧) 272.20 K, (⬓) 273.15 K. Solid blue lines show the stated expanded relative uncertainty of our experimental speed of sound values.

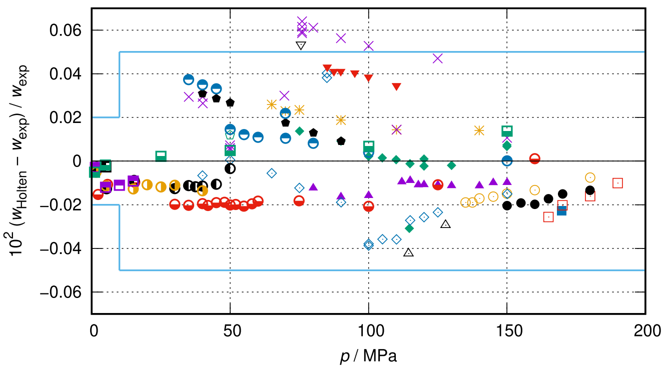

**Fig. 11.** Comparison of the experimental speed of sound measure with those predicted by the Holten et al. formulation. Symbols denote (■) 254.65 K, (□) 255.15 K, (●) 256.15 K, (○) 258.15 K, (▲) 260.15 K, (△) 261.20 K and 261.39 K, (◆) 262.15 K, (◇) from 263.14 K to 263.440 K, (▼) 263.65 K, (▽) 264.38 K, (✳) 264.65 K, (×) from 265.14 K to 265.65 K, (⬟) 266.15 K, (⬠) 266.65 K, (◓) 267.15 K, (◒) 268.15 K, (◐) 269.65 K, (◑) 270.65 K, (⬒) 271.65 K, (◧) 272.20 K, (⬓) 273.15 K. Solid blue lines show the stated expanded relative uncertainty of our experimental speed of sound values while the stated uncertainty for the Holten formulation is 0.1%.

The formulation of Holten et al., focused on metastable states, declared an uncertainty of 0.1%, and showed a better general agreement with results here reported, as shown in Fig. 11. Considering the absence of experimental measurements, it is remarkable that the deviations from the experimental results obtained here did not exceed 0.06% in the whole temperature and pressure range considered. Furthermore, we note that the deviations showed no major temperature or pressure dependence and were mainly limited to the range (60–120) MPa. In the light of this comparison, the uncertainty of the Holten et al. formulation could be probably reduced by a factor of two.

## 6. Conclusion

In this work, experimental speed of sound values in water were measured at temperatures between 254.65 K and 273.15 K and pressures up to 190 MPa. Accurate speed of sound measurements in the high-pressure region, and at low temperature and especially in metastable states, have been obtained with an estimated expanded relative uncertainty between 0.02% ($k = 2$) and, in the worst case, 0.05% ($k = 2$).

The measurements were carried out using the traditional double *pulse-echo* technique, also in $p - T$ ranges where experimental data were not yet available in the literature.

The results have been compared in stable states with the predictions of the reference equation for pure water (IAPWS-95 formulation) by Wagner and Pruß [2] and, in metastable state, with those calculated from the Equation of state for supercooled water by Holten's et al. [14] with resulting relative deviations that are within the uncertainties stated for the equations.

Moreover, the speed of sound results have been compared with the most recent results by Lin and Trusler [12] and by El Hawary and Meier [13] finding, in both cases, deviations always smaller than the combined uncertainties.

Work is in progress to complete the experimental speed of sound measurements in metastable ordinary water in a wider $p$–$T$ range: down to 250 K and pressure up to 350 MPa for states metastable with respect to ice Ih and ice III.

### CRediT authorship contribution statement

**S. Lago:** Writing – original draft, Validation, Supervision, Formal analysis, Data curation, Conceptualization. **M. Bertinetti:** Validation. **P.A. Giuliano Albo:** Writing – review & editing, Software, Investigation, Formal analysis, Data curation.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

The obtained data are available in the present paper.

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