

Determination of the Acoustic Nonlinearity Parameter in Liquid Water up to 250°C and 14 MPa

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Abstract— This work reports, for the first time, the direct measurement of sound speed in liquid water at temperatures up to 250°C and pressures up to 14 MPa. These measurements enabled the determination of the acoustic nonlinearity parameter, B/A, an important property of liquids. From an applications perspective, B/A determines the efficiency of devices that are based on acoustic nonlinear mixing. The objective of the present work was to use a specialized measurement cell for sound speed measurements and the determination of B/A in liquid water as a function of temperature and pressure. Sound speed was measured using Swept Frequency Acoustic Interferometry, while B/A was determined from the derivatives of the sound speed with respect to pressure and temperature. B/A at ambient pressure and temperature was determined to be 4.8, in good agreement with literature values. At 250°C and 14 MPa, B/A was found to be roughly twice its ambient temperature value.

Keywords—high temperature, water sound speed, nonlinearity

I. INTRODUCTION

Acoustic nonlinearity in fluids has several important technological applications. Specifically, harmonic imaging in biological media, as well as parametric sonar imaging rely on the nonlinearity of fluids [1-5]. A commonly used measure of a fluid's nonlinearity is the ratio B/A where A and B are the coefficients from the isentropic equation of state [6]:

$$P - P_0 = A \frac{\rho - \rho_0}{\rho_0} + \frac{B}{2} \left(\frac{\rho - \rho_0}{\rho_0} \right)^2 + \dots \quad (1)$$

One method of determining B/A is the 'thermodynamic method,' proposed by Beyer [6]. In this method, sound speed, c , measured over a range of temperatures and pressures are used to calculate the derivative of sound speed with respect to each of these two state variables. Combined with other thermodynamic properties of a liquid, specifically the density (ρ), the coefficient of volumetric expansion (β), and the isobaric specific heat (c_p), these derivatives can be used to calculate B/A [6]:

$$\frac{B}{A} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p} \right)_T + \frac{2c_0 T \beta}{c_p} \left(\frac{\partial c}{\partial T} \right)_p = \left(\frac{B}{A} \right)' + \left(\frac{B}{A} \right)'' \quad (2)$$

In Eqn (2) the pressure and temperature derivatives are taken at constant temperature and pressure, respectively, and the expressions are evaluated at the nominal sound speed, c_0 , and nominal density ρ_0 at an absolute (Kelvin) temperature T .

The B/A of water has previously been characterized up to 100°C [6-10]. However, emerging applications such as geothermal and petroleum industry downhole acoustic

nonlinear imaging require knowledge of B/A of fluids at higher temperatures and pressures. Applications in environments such as these, where temperatures are up to 250°C at depths of up to 10 km below ground in the continental US [11], partly motivated the present investigation. In this work, sound speeds in water were measured at 15 temperatures up to 250°C and at up to 11 pressures between the water vapor pressure and 13.8 MPa. Water sound speeds were determined using a high temperature/high pressure adaption of the Swept Frequency Acoustic Interferometry (SFAI) technique [12].

Section II reviews the SFAI technique and presents the specialized measurement cell and test environment. **Section III** describes the data analysis procedure to determine individual sound speeds and B/A. **Section IV** presents the results of the work and compares them with available literature values. Finally, **Section V** concludes the paper.

II. EXPERIMENTAL

A. SFAI Technique

Sound speed in water was measured using the SFAI technique [12] with a high temperature/high pressure-capable measurement cell detailed in [13]. The SFAI technique uses a pair of two opposing transducers, one acting as a transmitter and another one as a receiver, placed at the two ends of a fluid-filled resonant cavity. The frequency is swept between a region of interest and a resonance spectrum, consisting of multiple resonant frequencies, f_n , is recorded. Resonances are observed for acoustic waves with wavelengths, λ_n , satisfying the relationship $\lambda_n = 2L/n$ where n is the harmonic number and L is the liquid path length. Combining this condition with the wave relationship $c = \lambda_n f_n$, the sound speed of the liquid is given by the following expression:

$$c = 2L \frac{df_n}{dn} \quad (3)$$

B. Measurement Cell

The transducers used in this study have the following characteristics: 36° Y-rotated lithium niobate transducer with 5 MHz fundamental frequencies (Boston PiezoOptics, Inc., Bellingham, MA), with a diameter of 10 mm. The transducers are gold-plated in a coaxial configuration with an active area 7 mm in diameter. To protect the electrodes and crystals from the high temperature aqueous environment, each transducer was packaged in a stainless steel container constructed of a 1-1/3" Conflat (CF) blank flange, a 1-1/3" CF half-nipple, and a 2 mm-0.75" Swagelok reducing union (Fig. 1). Wells 13 mm

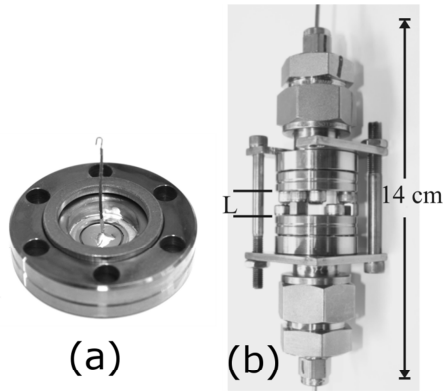


Figure 1(a) 5 MHz lithium niobate crystal bonded mounted in a blank 1-1/3" CF flange. (b) two stainless steel containers assembled to define measurement cell with cavity length L.

in diameter and 3 mm deep were machined into the CF blanks to accommodate the transducers. The well bottoms were smooth and parallel to the front surfaces of the flanges to within 25 μm . The transducers were bonded to the bottom of the wells using a high temperature epoxy (Epoxy H24 from Epoxy Technologies, Inc., Billerica, MA). Fig. 1(a) details one of the lithium niobate crystals bonded into a well in the 1-1/3" CF blank flange. The electrical signal was carried to and from the transducers using a stainless steel sheathed coaxial cable that had an outer diameter of 2 mm. The coaxial cable is rated to 600°C (THERMOCOAX, Inc). A Swagelok compression fitting was used to seal the stainless steel container against the coaxial cable. Fig. 1b shows how the two stainless steel containers were arranged facing each other to form the measurement cell. The front faces of the CF blank flanges defined the boundaries of the resonant cavity. The physical dimension of the resonant cavity is $L=8.85$ mm (Fig. 1b). The measurement cell had an overall length of 14 cm.

C. Sample Environment

The measurement cell was placed inside a pressure vessel rated to 500°C and 5000 PSI (model# 4681, Parr Instrument Company, Moline, IL). The 1 liter pressure vessel was filled with 700 mL of degassed deionized water. The measurement cell itself occupied a volume of roughly 100 mL with the headspace of the vessel consisting of nominally whole air. The two signal carrying coaxial cables between the measurement cell and the data acquisition electronics were fed into the pressure vessel using Grafoil gland compression fittings (MHM2 series, Conax Technologies, Buffalo, NY). To control the hydrostatic pressure in the test environment, the headspace was pressurized with N_2 using a pressure amplifier (Model: AAD-30, Haskel International, Inc., Burbank, CA) arranged in line with a compressed gas cylinder. For measurements at temperatures between 80°C and 250°C, the pressure vessel was placed in a fitted furnace. At temperatures below $\sim 80^\circ\text{C}$, the furnace was not efficient at stabilizing the temperature of the vessel due to the large thermal mass of the system. For these lower temperatures, the vessel was immersed in a 4 gallon temperature controlled water bath.

D. Data Collection

Data were collected at 15 temperatures between 20°C and 250°C. At each temperature, measurements were recorded at 11 equally spaced pressures between the ambient water vapor pressure and 13.8 MPa. Due to expansion and compression of the gas in the headspace of the test environment, the temperature of the water changed by up to a couple degrees Celsius between the ambient and 13.8 MPa data points, with the latter having higher temperatures. The temperature of each data point was recorded with a precision of $\pm 0.1^\circ\text{C}$ and an accuracy of 1.1°C using a type-J thermocouple positioned in the pressure vessel to measure the water temperature inside the resonant cavity. The pressure at each data point was recorded with a precision of ± 0.5 psig (3.4 kPa) using a 0-5000 psig (34.5 MPa) pressure transducer (Model PX309-5KG5V, Omega Engineering, Inc.) with a manufacturer-reported accuracy of 13 psig (90 kPa).

The resonance spectra were recorded using a vector network analyzer (Model Bode 100, OMICRON electronics Corp. USA, Houston TX). At each temperature and pressure, 6401 points were recorded with a 1 kHz receiver bandwidth between 1 MHz and 8 MHz at a source power of 0 dBm.

III. ANALYSIS

A. Sound Speed Determination

Sound speed was determined using Eqn. (3). Figure 2 shows an example of a resonance spectrum with 20 f_n indicated with open circles. The resonant cavity walls, in this case the stainless steel of the CF blank flanges, also have their own resonant frequencies that are spaced much more widely in the frequency domain than the fluid peaks due to the high speed of sound in steel. At the wall thickness mode resonant frequencies, energy coupling between the walls and the fluid can lead to errors in the determined df_n/dn for the fluid [12]. For this reason, fluid resonances in the vicinity of wall resonances were not selected for df_n/dn determination as can be seen in Fig. 2.

B. Calculation of B/A

As seen in Eqn (2), to determine B/A, it is necessary to know how the speed of sound varies with temperature and pressure. To determine dc/dp , the measured sound speeds

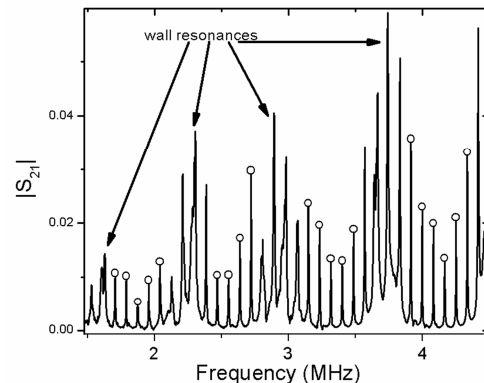


Figure 2. An example SFAI resonance spectrum. 20 water resonances used for the determination of df_n/dn are indicated with open circles.

were binned by “nominal temperature” into 15 groups. Because the temperature of the vessel drifted by up to a couple degrees Celsius between measurements at different pressures, it was necessary to account for this small temperature difference in determining the pressure dependence of sound speed. For a small temperature range it can be safely assumed that the relationship is linear in temperature. The data in each bin were fit with a polynomial that was linear in temperature and quadratic in pressure:

$$c(T, P) = a_{00} + a_{10}T + a_{01}P + a_{01}P^2. \quad (4)$$

The a_{ij} coefficients were determined using a least squares fit with two independent variables. After each fit, measured data points lying more than two standard deviations away from the polynomial fit were discarded as outliers and the polynomials were recalculated, if necessary. Additionally, all data points in the 195°C bin were discarded because of poor fit and high discrepancies with available literature data [14]. The a_{ij} coefficients enabled the calculation of dc/dp at each temperature and pressure. To determine dc/dT , the measured sound speeds, less the outliers discarded in the pressure polynomial fit described above, were binned into groups having the same pressure. A polynomial that was sixth order in temperature was then fit to each set of isobaric data and differentiated to determine dc/dT at each temperature and pressure combination:

$$c(T, P) = a_{00} + a_{10}T + a_{20}T^2 \dots + a_{30}T^3 + a_{40}T^4 + a_{50}T^5 + a_{60}T^6. \quad (5)$$

A sixth order fit was chosen because it modeled the temperature behavior more accurately than lower order fits and was not improved when replaced with a higher order fit. Because the literature contains no directly measured water sound speeds over the entire temperature and pressure range studied in this work, sound speeds calculated from an internationally accepted standard equation of state for water, the IAPWS-IF97 formulation [14], were used as a basis for comparison. These predicted sound speeds were calculated at each of the temperatures and pressures for which measurements were made in this work. To determine the temperature and pressure dependence of the IAPWS data, the predicted sound speeds were fit with a polynomial that is sixth order in temperature and third order in pressure:

$$c(T, P) = \sum_{i=0}^6 \sum_{j=0}^3 a_{ij} P^j T^i. \quad (6)$$

The order of this polynomial was chosen since it represented the lowest order polynomial that accurately fit the sound speeds.

The density, ρ , isobaric specific heat capacity, c_p , and the volumetric coefficient of thermal expansion, β , needed to determine B/A were calculated from the IAPWS-IF97. These quantities were combined with dc/dp and dc/dT from Eqns (4-5) to calculate B/A for the measured sound speeds. Similarly, these thermodynamic quantities were combined with derivatives calculated from Eqn (6) to determine B/A for the IAPWS predicted sound speeds.

IV. RESULTS

A. Sound Speed

The measured sound speeds were compared to the IAPWS sound speeds at each temperature and pressure for which a measurement was made. A plot of the percent difference between the two data sets ((IAPWS-measured)/measured*100) be seen in Fig. 3. Of the 166 sound speeds measured, 58% were within 0.2% and 83% were within 0.3% of the IAPWS-IF97 predicted sound speeds. The uncertainty in the IAPWS sound speeds is quoted at 0.4%, which is ~4 m/s for the sound speeds considered in this study. The uncertainty in the measured sound speeds reported here is primarily due to the accuracy of the temperature measurement of $\pm 1.1^\circ\text{C}$. In the vicinity of 70°C , sound speed varies very little with temperature and so inaccuracy in temperature measurement does not have a large effect on the determined $c(P,T)$. However, at higher and lower temperatures, sound speed can change with temperature by 3-4 m/s/ $^\circ\text{C}$ and so inaccuracies in temperature measurements have a more pronounced effect on the accuracy of $c(P,T)$.

B. Determined B/A

The B/A values in water at ambient pressure up to 85°C are compared to available literature values in Fig. 4. The values found in this study were all within 10% of both the IAPWS predicted values as well as those determined in [6]. Other available values for B/A that are quoted in [6, 9] are plotted for comparison. While most 20°C values of B/A are very close to 5, two points above 6.5 show the uncertainty in this derived quantity. B/A as a function of pressure for selected temperatures are compared with those from the IAPWS sound speeds in Fig. 5. As a general observation, B/A tends to increase with both increasing temperature and pressure. The 153°C data set is unique in that the B/A calculated from measured values as well as the IAPWS-IF97 sound speeds show a decreasing trend with increasing pressure. For most of the B/A values presented in Fig. 5, those calculated from measured and predicted sound speeds are within 15% with the worst case in the entire data set (not shown), being ~75% different. This particular difference is slightly higher than the

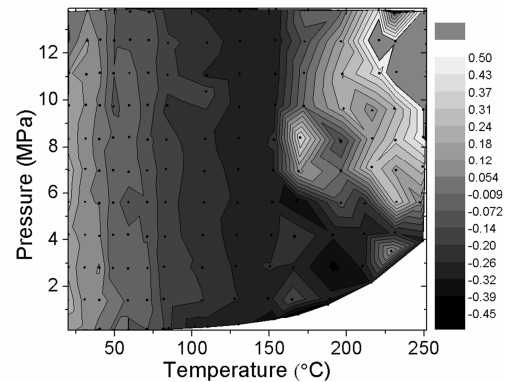


Figure 3. Map of Temperature-Pressure space showing the difference between IAPWS-IF97 predicted sound speeds and the sound speeds measured in this work. Filled circles denote measurement points.

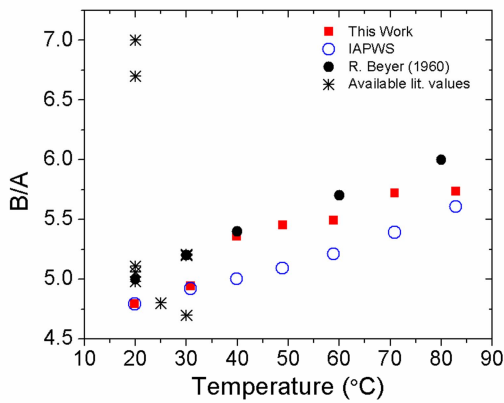


Figure 4. B/A values for water at ambient pressure up to 85°C. The values determined in this work are within 10% of the IAPWS values and those reported in [6]. Other available values quoted in [6] and [9] are also plotted for comparison.

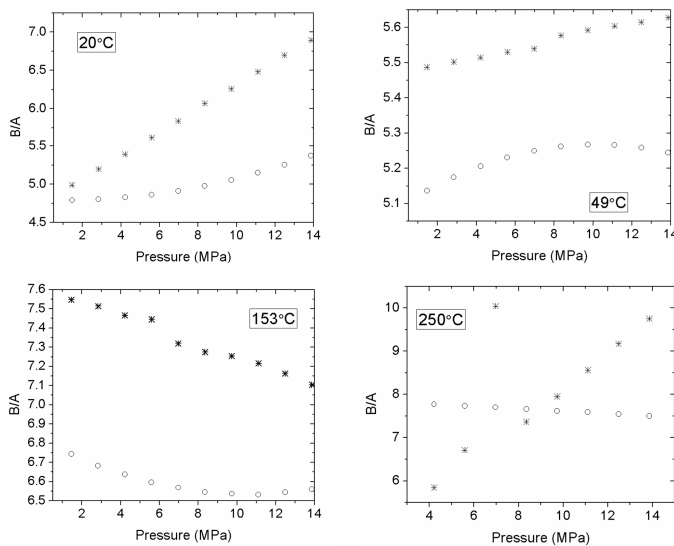


Figure 5. B/A calculated from measured data (asterisks) as well as from the IAPWS-IF97 steam tables (open circles) as a function of pressure for four selected temperatures.

spread in B/A values at room temperature (see Fig. 4), reflecting the difficulty in extracting this parameter.

For water, B/A'' in Eqn (2) contributes only ~5% of the total value of B/A; B/A is thus extremely sensitive to the determination of dc/dp . For the pressure range considered in this study, the speed of sound in water changes by only on the order of 20 m/s. A 2 m/s net error in sound speed over this range thus directly contributes a 9.5% error in B/A. Given the uncertainty in the IAPWS sound speeds and the uncertainty in the temperature measurement in this work, all B/A values determined from measured sound speeds agree with those determined from IAPWS sound speeds.

V. CONCLUSIONS

This work, for the first time, has reported on the direct measurement of sound speed in liquid water at temperatures

up to 250°C and pressures up to 14 MPa. The entire measured sound speed set was found to be within 1% of sound speeds predicted by the IAPWS-IF97 international standard, with 85% of measured data points being within 0.3% of the predicted sound speeds. Values for the parameter of nonlinearity, B/A, for liquid water were calculated from both the measured and predicted data set and found to be in general agreement with each other. At 20°C, B/A was determined from measured data to be 4.8 which is in agreement with previous literature values. B/A was found to generally increase with both increasing temperature and pressure. The maximum value of B/A determined from measured sound speeds was close to 10. The IAPWS-IF97 sound speeds led to a 20% lower maximum B/A near 8.

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