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# Fully automatized apparatus for determining speed of sound for liquids in the temperature and pressure interval (283.15–343.15) K and (0.1–95) MPa

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ABSTRACT

An instrument for determining the speed of sound as a function of temperature and pressure for liquids is described. It was totally automatized: pressure and temperature values are controlled and time of flight of the ultrasonic wave data were acquired using a digital system which automatically made all required actions. The instrument calibration was made only at atmospheric pressure using high quality data of water and methanol. For higher pressures, the calibration parameters were predicted using a model for the high pressure cell, through finite-element calculations (FEM), in order to realistically determine the changes in the cell induced by the compression. Uncertainties in pressure and temperature were 20 mK and 0.1 MPa, respectively and in speed of sound it was estimated to be about 0.1%. The speeds of sound for water, methanol, hexane, heptane, octane, toluene, ethanol and 1-propanol were determined in the temperature and pressure ranges (283.15–343.15) K and (0.1–95) MPa. Comparison with literature data reveals the high reliability of the experimental procedure.

## 1. Introduction

From the point of view of the thermodynamics of liquids, the speed of sound is a very important magnitude, since it is directly related to compressibility. In fact, there is a direct relation between them by means of the widely known Laplace's equation:

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_S = \frac{1}{\rho \kappa_S} \tag{1}$$

where $c$, $\rho$, $p$, $S$ and $\kappa_S$ denote speed of sound, density, pressure, entropy and isentropic compressibility [1]. Moreover, accurate $c$ data against temperature and pressure allow the calculation of many other thermophysical properties –usually densities, isobaric and isochoric heat capacities, isothermal compressibility and isobaric thermal expansivity–to be performed. The start point is knowing some of these magnitudes at one reference pressure –usually atmospheric– and exploiting the relations that link these magnitudes with the speed of sound through numerical integration or derivation of the experimental data. In this context, many calculation schemes have been developed in order to maximize the precision of the obtained data [2–6]. For enough accurate experimental values, some of these calculation procedures give very good results, in some cases even better than those directly determined using the available experimental methodologies.

Besides the interest that high quality speed of sound could have from a purely empirical point of view, $c$ is one of the key magnitudes used in the field of equations of state (EoS), which is the main way for predicting and understanding fluid thermodynamics. Most theoretical and empirical EoS use this quantity to obtain the model parameters and/or to check the EoS accuracy. In this context, availability of highly precise speed of sound data is of major need in order to improve the reliability of EoS.

The speed of sound is usually determined by evaluating the time that an ultrasonic wave lasts travelling some length occupied by the sample. Since there are very precise methods for measuring times –instruments with a precision of nanoseconds are easily available- this magnitude is a widely measured thermodynamic quantity. Relative uncertainties better than 0.5% are easily obtained in extended temperature and pressure ranges.

In this work a novel experimental set-up for accurate speed of sound measurements is presented. It is based on a cell developed some years ago by Professor Rebelo's research group, from the Universidade Nova de Lisboa [7]. The equipment was fully

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automatized, which allowed a great amount of highly precise data in wide temperature and pressure ranges to be quickly obtained, with typical times of fifteen hours for collecting all data for one sample. Since available high pressure speed of sound values for most liquids are of significant lower quality than atmospheric pressure ones, it would be desirable to calibrate the instrument only with data at atmospheric pressure. A new calibration methodology was developed to this end, based on calculations of the cell deformation under pressure using finite elements methods. Therefore, only two standards at atmospheric pressure were needed. Data at high pressure for water was obtained and compared with reference, extremely reliable data, in order to check this calibration methodology. The uncertainty evaluation of the experimental procedure was performed using standard uncertainty calculations [8,9] over the whole experimental range. In order to check the reliability of the measuring system and uncertainty estimation, speed of sound measurement for a set of liquids (hexane, heptane, octane, toluene, methanol, ethanol and 1-propanol), for which *c* is known with high precision, were made, and comparison with literature data was carried out.

**Table 1**
Supplier mass fraction purity (*w*), source and purification method of the samples.

| Liquid | *w* | Origin | Purification method |
|---|---|---|---|
| Water | – | MilliQ | None |
| Toluene | >0.998 | Sigma-Aldrich | None |
| Hexane | >0.99 | Scharlau | None |
| Heptane | >0.99 | Sigma-Aldrich | None |
| Octane | >0.995 | Fluka | None |
| Methanol | >0.9999 | Scharlau | Molecular sieves |
| Ethanol | >0.999 | Scharlau | Molecular sieves |
| 1-Propanol | >0.997 | Sigma-Aldrich | Molecular sieves |

**Table 2**
Density and refractive index of the liquids of this work ($\rho$ and $n_D$) at 298.15 K and $p = 0.1$ MPa compared with literature data ($\rho_{Ref}$ and $n_{D,Ref}$) [10].[a]

| Liquid | $\rho$/g·cm$^{-3}$ | $\rho_{Ref}$/g·cm$^{-3}$ | $n_D$ | $n_{D,Ref}$ |
|---|---|---|---|---|
| Water | 0.9970 | 0.997047 | 1.3326 | 1.33250 |
| Toluene | 0.8622 | 0.86219 | 1.4940 | 1.49413 |
| Hexane | 0.6549 | 0.65484 | 1.3723 | 1.37226 |
| Heptane | 0.6795 | 0.67946 | 1.3852 | 1.38511 |
| Octane | 0.6984 | 0.69862 | 1.3951 | 1.39505 |
| Methanol | 0.7865 | 0.78637 | 1.3263 | 1.32652 |
| Ethanol | 0.7851 | 0.78493 | 1.3593 | 1.35941 |
| 1-Propanol | 0.7995 | 0.79960 | 1.3830 | 1.38370 |

[a] Standard uncertainties are: For density measurement $u(T) = 0.005$ K, $u(p) = 0.002$ MPa, and $u(\rho)/\rho = 0.1\%$ and for refractive index measurement $u(T) = 0.020$ K, $u(p) = 0.002$ MPa, and $u(n_D)/n_D = 0.1\%$.

## 2. Experimental

A description of the sources and purity of all studied liquids is given in Table 1. In order to check its purity, density and refractive index were measured in a DMA5000 densimeter and Mettler Toledo RE50 refractometer. The obtained values compared with literature are given in Table 2.

The speed of sound was determined from the time of flight of an ultrasonic wave emitted by a piezoelectric located at one end of the cell, which is received by other twin piezoelectric located at the other side. The cell is able to support 100 MPa and was designed and constructed by Professor Rebelo's research group at the Universidade Nova de Lisboa. Fig. 1 shows its scheme; further details can be found elsewhere [7]. The piezoelectric was excited by a sinusoidal 1-wave burst of 16 V at 1.5 MHz, with a repetitive period of 5 ms using a voltage source model 8551 from Tabor Electronics. After passing through the liquid, the wave was detected by the other piezoelectric. The time of flight was obtained using a 6020 counter, also from Tabor Electronics, which takes the mean value over 1000 reads every 5 s. Uncertainty in time of flight is estimate in 2.5 ns. Temperature control was made using a Polyscience thermostat (model 9110), being the temperature probe (PRT100) located at the cell, which is submerged in a water/ethyleneglycol bath. Uncertainty in temperature is estimated to be about 20 mK. Pressure control was performed using a DC motor coupled with a pressure generator (model 50-6-15 from HiP company) and a S-100 transducer from Wika. At pressures above 0.1 MPa, uncertainty is estimated to be around 0.10 MPa, while stability is better than 0.07 MPa; at $p = 0.10$ MPa, uncertainty is 0.02 MPa. A computer program was developed in order to control temperature and pressure and to acquire time of flight data. Very restrictive stability criteria (typical fluctuations in $T$ and $p$ below 0.003 K and 0.05 MPa) were applied and the final datum was obtained by taking the mean value of 100 data, facts which maximize the accuracy of the procedure. Fig. 2 shows a scheme of the measurement system. Speed of sound was obtained at each temperature using the equation:

$$t_{of} = t_0 + \frac{l(p,T)}{c(p,T)} \tag{2}$$

where $t_{of}$, $c$, $t_0$ and $l$ denote: time of flight, speed of sound, delay time and acoustic length. $t_0$ is due to the time that the ultrasonic wave lasts going through steel walls of the cell, the time needed to excite the piezoelectrics, and other effects due to electronics. In principle, $t_0$ and $l$ are both pressure and temperature dependent, fact which would imply the need of speed of sound reference data for the standard liquids at all measurement temperatures and pressures. This is an important uncertainty source: data at atmospheric pressure is known with high accuracy for a large set of substances,

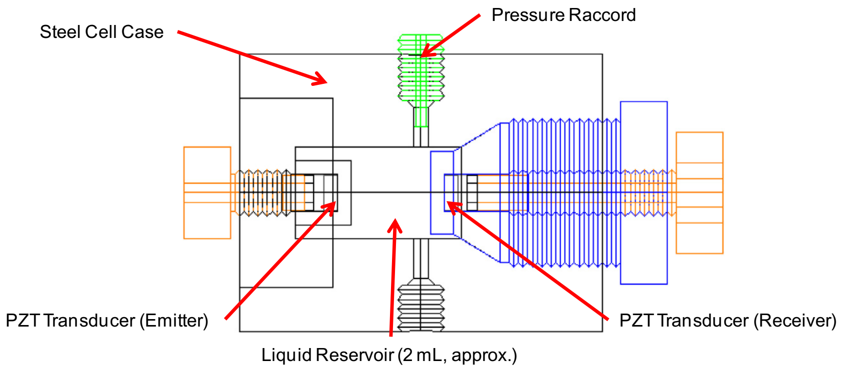

**Fig. 1.** Cell scheme.