The acoustic nonlinearity parameter in Fluorinert up to 381 K and 13.8 MPa

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Abstract: This work reports on the determination of the acoustic nonlinearity parameter, B/A, from measured sound speed data, in Fluorinert FC-43 at temperatures up to 381 K and pressures up to 13.8 MPa using the thermodynamic method. Sound speed was measured using Swept Frequency Acoustic Interferometry at 11 pressures between ambient and 13.8 MPa along 6 isotherms between ambient and 381 K. Second-order least-squares polynomial fits of measured sound speeds were used to determine temperature and pressure dependence. A room temperature B/A = 11.7 was determined and this parameter was found to increase by a factor of 2.5 over the temperature/pressure range investigated.

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1. Introduction and background

Accurate measurements of sound speed as a function of temperature and pressure can be used to extract the parameter of nonlinearity, B/A, of a medium.[1–4] Knowledge of B/A in a medium has important technological implications as this parameter determines the efficiency with which higher harmonics as well as sum and difference frequencies, useful in applications such as nonlinear acoustics-based imaging, can be generated in a medium.[5] For applications in high temperature or high pressure environments, such as those typically found in geothermal or petroleum wells, it is necessary to understand how the nonlinearity of media change with temperature and pressure. Such knowledge enables the design of nonlinear acoustics-based devices at the temperatures and pressures characteristic of these environments.

In this work, sound speed was measured in Fluorinert FC-43 over a 100 K temperature span and a 14 MPa pressure span, enabling the determination of B/A over this same *P-T* space. Previous studies have shown that Fluorinerts are acoustically highly nonlinear near room temperature with B/A values between 11 and 13 (Refs. 3, 6, and 7) but values at elevated temperatures and pressures have not been reported. The upper temperature limit was chosen to be as high as possible while maintaining a conservative margin of safety below 473 K at which point FC-43 decomposes into hydrogen fluoride and perfluoroisobutylene, both of which are toxic. The pressure limit was determined by the available experimental setup.[8]

Sound speed was measured using the Swept Frequency Acoustic Interferometry (SFAI) technique.[9] The SFAI setup used in this work was developed especially for high temperature and high pressure applications and has previously been shown to yield a precision significantly better than 0.1%.[8]

In this work, B/A was determined from the measured sound speeds using the thermodynamic method:[1]

$$\frac{B}{A} = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_s = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_T + \frac{2c_0 T\beta}{C_p}\left(\frac{\partial c}{\partial T}\right)_P = \left(\frac{B}{A}\right)' + \left(\frac{B}{A}\right)''. \tag{1}$$

Equation (1) relates the sound speed, c, to the state variables entropy (S), temperature (T), and pressure (P). Sound speed was measured as a function of temperature and pressure while the density (ρ), volumetric coefficient of thermal expansion (β), and isobaric specific heat (C_p) were determined from manufacturer data sheets (3M Company, St. Paul, MN).

2. Experimental

Sound speed was determined as a function of temperature and pressure using the SFAI technique and a specially designed high temperature, high pressure-capable resonance

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cell. The resonance cell and the SFAI technique are detailed in Refs. 8 and 9, respectively. Briefly, SFAI determines the sound speed, c, of a medium by measuring multiple equally-spaced resonances, f_n, in a resonant cavity with a relevant acoustic path length, L. The experimentally determined f_n and L are related to the sound speed as follows:

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

In this study, the sample environment consisted of a 1-liter high pressure vessel rated to 34.5 MPa and 873 K (model #4681, Parr Instrument Company, Moline, IL) with temperature and pressure controlled as described in Ref. 8. The pressure vessel was filled with 700 ml of Fluorinert FC-43. The resonance cell, itself occupying a volume of approximately 100 ml, was completely immersed in the FC-43 inside the pressure vessel. The temperature of the FC-43 was measured with a precision of 0.1 K and an accuracy of 1.1 K using a type-J thermocouple (Model M8MJSS-M2-U-250, Omega Engineering, Inc.) with the sensing junction placed immediately next to the resonant cavity. The pressure inside the vessel was measured using a pressure transducer with an accuracy of ±90 kPa (Model PX309–5 KG5V, Omega Engineering, Inc.).

Data were collected at six temperatures between laboratory ambient and 381 K: T = [294, 313, 323, 331, 354, 381] K. At each temperature, data were collected at pressure increments of 1.379 MPa between the vapor pressure of FC-43 and 13.79 MPa. Before data collection could begin, the pressure vessel was brought to the desired temperature and allowed to equilibrate until the temperature read by the thermocouple was stable to within 0.1 K over a period of several minutes. Once equilibrium was achieved, the system was raised to a maximum pressure of 13.79 MPa by pressurizing the 200 ml headspace in the pressure vessel using a pressure amplifier (Model AAD-30, Haskel International, Inc., Burbank, CA) with nitrogen gas from a cylinder. Pressurizing (and subsequent venting of) the headspace in the vessel caused the temperature in the FC-43 to change by up to several kelvins and so the system was again allowed to thermally equilibrate after pressurizing. After system equilibration was achieved, an SFAI spectrum was collected using a vector network analyzer (Model Bode 100, Omicron Electronics Corp., Houston, TX). Following each measurement, the pressure in the system was reduced by 1.379 MPa by bleeding the gas in the headspace through a needle valve over the course of approximately 1 min. After thermal equilibration, another spectrum was collected and this sequence of lowering the pressure, equilibrating, and collecting a spectrum was reiterated until the system was at the vapor pressure of FC-43.

Sound speed and density data were also collected at laboratory ambient pressure and at temperatures up to 343 K using a commercially available density and sound speed meter (Model DSA 5000 M, Anton Paar GmbH). The FC-43 sound speed, $c = 657.4 \pm 0.5$ m/s, at 294 K measured by the DSA 5000 M, was used to calibrate the path length, $L = 8.796 \pm 0.007$ mm, of the resonance cavity [Eq. (2)]. This path length was adjusted for thermal expansion using a linear thermal expansion coefficient of 17.2×10^{-6}/K for the stainless steel spacer in the measurement cell.[8,10]

3. Data analysis

Sound speed was determined from the SFAI spectrum using Eq. (2) and the procedure described in Ref. 8. By using 20 to 30 resonance peaks, a precision of 0.01% to 0.07% in the determined sound speed was achieved, with a mean uncertainty of 0.03% or ~0.2 m/s.

Using the complete set of measured sound speeds, the data were binned into 6 isothermal data sets at T = 294, 313, 323, 331, 354, 381 K. For each isotherm, a polynomial was used to fit the data that was linear in temperature and second order in pressure. These polynomial fits were used to calculate dc/dp, needed for the determination of B/A′ [Eq. (1)]. The linear temperature term was used to account for small changes in temperature as the system was pressurized or vented, as mentioned above. Statistics for each fit were noted and data points lying more than two standard deviations (2σ) from the fit were discarded as outliers and the polynomial was re-fit. This procedure was repeated until all data points were within 2σ of the fit. Of the 75 sound speeds measured, 6 were discarded based on this criterion. This number of 2σ outliers is approximately what is expected for normally distributed random errors and the outlying data points likely arise from the uncertainties in the temperature and pressure measurements described in Sec. 2. The rationale behind excluding these points from the determination of dc/dp was to ensure that the derivative could be quantified as accurately as possible. Since B/A for FC-43 is 89% attributable to B/A′, as shown below, it is important that one has high confidence in this quantity.

The remaining data, without the discarded outliers, were then binned into 11 equally spaced isobars between ambient pressure and 13.79 MPa. A polynomial that was linear in pressure and quadratic in temperature was fit to each set of isobaric data and the derivatives $\partial c/\partial T$ were determined from these fits. The order of polynomials used to fit the isothermal and isobaric data were chosen to be as low as possible to accurately capture the behavior of the sound speed with respect to these parameters.

The additional quantities needed for the calculation of B/A (i.e., C_p, ρ, and β) were determined from manufacturer documentation (3M Company). Since there was no information available that relates these quantities to pressure, they were assumed to be constant in pressure. The values of each thermodynamic property and derivative appearing in Eq. (1) were calculated at every combination of isobar and isotherm indicated above. Since measured sound speeds did not coincide with the exact temperatures/pressures for which B/A was being calculated, the c values needed to apply Eq. (1) were determined from the polynomial fit to the isothermal data determined above.

4. Results and discussion

4.1 Sound speed

The sound speeds measured using the SFAI technique as a function of temperature at laboratory ambient pressure are compared with those measured using the DSA 5000 M and those reported in Ref. 3 in Fig. 1(a). The measurement precisions are ∼0.2 m/s for the SFAI data and 0.5 m/s for the DSA 5000 M data with error bars smaller than the data markers. A larger uncertainty in the SFAI measurement arises from the 1.1 K uncertainty in the temperature measurement, though the horizontal error bars associated with this uncertainty are also invisible in Fig. 1(a). Sound speed can be seen to decrease by ∼2.6 m/s/K over this temperature range.

Figure 1(b) presents all of the sound speeds measured in this work as a function of temperature and pressure. As expected, c is found to decrease with temperature at all pressures and increase with pressure at all temperatures. The highest sound speed determined in this work was 722.4 m/s at a temperature of 295 K and a pressure of 13.79 MPa. At a temperature of 378 K and a pressure of 1.379 MPa, c was found to be 39% lower with a minimum value of 443.8 m/s.

4.2 Determined B/A

At laboratory ambient conditions of 295 K and 75.8 kPa, B/A was determined to be 11.7. This value can be compared with previously published values of 12.85 (Ref. 3) and 13.2 in both Refs. 6 and 7, with the latter using the finite amplitude method to determine B/A. Studies that determine B/A using the thermodynamic and finite amplitude methods often report uncertainties of 5% and 10%, respectively.[11] Depending on the medium being studied and the dependence of sound speed on temperature and pressure, larger uncertainties in the thermodynamic method are plausible given that this method calculates B/A from derivatives. The upper limit of the uncertainty in B/A

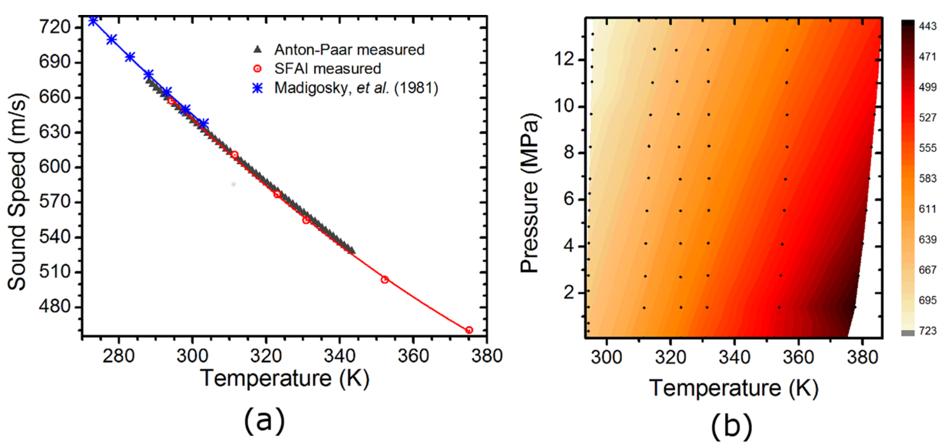

Fig. 1. (Color online) (a) SFAI-determined sound speeds plotted with those determined by the Anton-Parr DSA 5000 M and reported in Ref. 3 at laboratory ambient pressure. Vertical and horizontal error bars for the SFAI-measured data are smaller than the data markers. (b) SFAI-determined sound speeds in m/s in FC-43 over the temperature-pressure space studied. Closed circles represent points in P-T space at which sound speeds were measured.

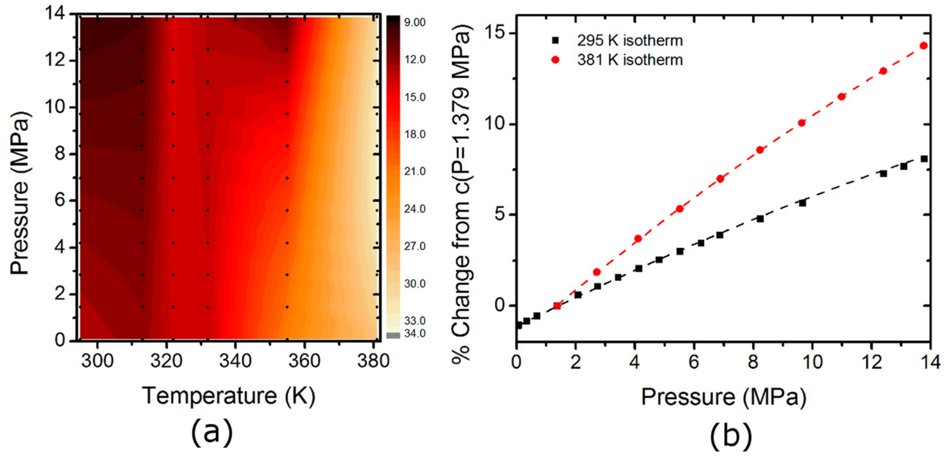

Fig. 2. (Color online) (a) B/A determined from SFAI-measured sound speeds over the temperature-pressure space studied. Closed circles represent points at which B/A was calculated. (b) Percent change in measured sound speed as a function of pressure, relative to the 1.379 MPa sound speed, for two different isotherms: 295 and 381 K, with second order polynomials fitted. The slope of these data vs pressure is the largest contributor to determined B/A values.

determined in this work is estimated to be 9% and is largely attributable to the uncertainty in the temperature measurement described in Sec. 4.1. B/A′ was determined to be 13.0 at laboratory ambient conditions, with B/A″ = −1.3 contributing 11% to the overall nonlinearity. This strong dependence on B/A′, and thus $\partial c/\partial p$, justifies the decision to discard a small fraction of data points to enable determination of $\partial c/\partial p$ as accurately as possible. It is interesting to note that the B/A′ = 13.0 contribution determined here, where the pressure changes are taken to be isothermal rather than isentropic, agree very well with the isentropic pressure derivative of sound speed reported in Ref. 6. The 11% contribution of B/A″ determined in this work, while small, is considerably larger than the 2.7% contribution of B/A″ to the overall B/A of water[1] and cannot be neglected.

Figure 2(a) presents B/A in FC-43 as a function of temperature and pressure over the entire parameter space studied. An increase in B/A is observed with increasing temperature and the parameter is seen to decrease slightly with pressure. The overall value of B/A is largely attributable to the B/A′ term. The contribution of B/A″ remains small over all temperatures and pressures probed with a value typically between −1.4 and −0.5. For B/A, the most notable point is the large increase of this parameter with temperature, particularly for the 355 and 381 K isotherms. At 381 K, B/A is ∼30, or approximately 2.5 times its room temperature value. This increase comes almost entirely from an increase in $\partial c/\partial p$ along the respective isotherms. Figure 2(b) plots the percent change in the 295 and 381 K isothermal data sets, relative to their 1.379 MPa values, as a function of pressure. In the figure, each sound speed has been adjusted to an effective temperature of either 295 or 381 K by assuming a temperature derivative of c of $\partial c/\partial T = -2.6$ m/s/K [see Fig. 1(a)]. This step was required since the data, as collected, were not all at exactly the same temperature, as noted above. As seen in the figure, the pressure derivative of c is ∼2.5 × higher for the 381 K data, largely explaining the increase in B/A′ and, consequently, B/A.

5. Conclusions

This paper has reported on the measurement of sound speed in Fluorinert FC-43 with a precision of 0.05% over a 14 MPA range of pressures and a 100 K temperature span using SFAI. Sound speed was found to increase with pressure and decrease with temperature, as expected. From the measured sound speeds, the parameter of acoustic nonlinearity, B/A, was calculated over the same *P-T* space. The laboratory ambient B/A = 11.7 is in agreement with previously published values. Most interestingly, B/A was found to increase by a factor of 2.5 to ∼30 at 381 K. This result is promising for the development of acoustical nonlinear-based imaging technologies in high temperature environments.

Acknowledgments

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