Leander Claes*, Lars Moritz Hülskämper, Elmar Baumhögger, Nadine Feldmann, René Spencer Chatwell, Jadran Vrabec, and Bernd Henning

Acoustic absorption measurement for the determination of the volume viscosity of pure fluids

Messverfahren für die akustischen Absorption zur Bestimmung der Volumenviskosität reiner Fluide

Abstract: A realistic description of fluid mechanical and acoustic processes requires the volume viscosity of the medium to be known. This work describes how the volume viscosity of pure fluids can be determined by measuring acoustic absorption with the pulse-echo method. The challenge in realizing such a measurement method lies in the separation of the different dissipative effects that superimpose on absorption. Diffraction effects ultimately cause a dissipation of acoustic energy and acoustic reflector surfaces have a small, but finite transmission coefficient. Further, influences of the transducer (in particular its frequency response), as well as the system's electrical components have to be taken into account. In contrast to the classical approach relying on the amplitude ratio, the absorption is determined by the moments of the amplitude spectrum. The measurement system applied is originally designed for precision measurements of the sound velocity by means of the propagation time difference of two acoustic signals.

Keywords: Acoustic absorption, volume viscosity, ultrasound.

Zusammenfassung: Eine realitätsnahe Beschreibung strömungsmechanischer wie akustischer Vorgänge setzt voraus, dass die Volumenviskosität des Mediums bekannt ist. In diesem Beitrag wird gezeigt, wie sich die Volumenviskosität reiner Fluide über eine Messung der akustischen Absorption durch Puls-Echo-Messungen ermitteln lässt. Die Herausforderung bei der Realisierung eines derartigen Messverfahrens liegt in der Trennung der unterschiedlichen dissipativen Effekte, welche der Absorption im Fluid überlagert werden. Beugungseffekte endlich großer Schallwandler bedingen zum Beispiel eine Dissipation der akustischen Energie im Raum. Im Gegensatz zur klassischen Methode über das Amplitudenverhältnis, wird die Absorption über die Momente des Amplitudenspektrums bestimmt. Als Messsystem dient dabei ein Aufbau, welcher zur präzisen Messung der Schallgeschwindigkeit über die Laufzeitdifferenz zweier akustischer Signale ausgelegt ist.

Schlüsselwörter: Akustische Absorption, Volumenviskosität, Ultraschall.

*Corresponding author: Leander Claes, Measurement Engineering Group, Paderborn University, Warburger Straße 100, 33098 Paderborn
Lars Moritz Hülskämper, Nadine Feldmann, Bernd Henning, Measurement Engineering Group, Paderborn University, Warburger Straße 100, 33098 Paderborn
Elmar Baumhögger, Thermodynamics and Energy Technology, Paderborn University, Warburger Straße 100, 33098 Paderborn
René Spencer Chatwell, Jadran Vrabec, Thermodynamics and Thermal Separation Processes, Technische Universität Berlin, Ernst-Reuter-Platz 1, 10587 Berlin

1 Motivation

Despite the fact that the volume viscosity is one of the thermodynamic properties of the Navier-Stokes equation, there is only a very limited amount of experimental data available for a few selected fluids. Acoustic absorption measurement is the most widespread method to sample the volume viscosity. If acoustic absorption α can be measured experimentally, the volume viscosity μ_v can be determined, given that several other quantities of the fluid are known and the angular frequency ω is sufficiently small [22]:

$$\alpha(\omega) = \frac{\omega^2}{2\rho c^3}\left(\frac{4}{3}\mu_\mathrm{s} + \mu_\mathrm{v} + \frac{c_\mathrm{p} - c_\mathrm{v}}{c_\mathrm{p} \cdot c_\mathrm{v}}\nu\right) = \frac{\omega^2}{2\rho c^3}\mu, \quad (1)$$

where ρ constitutes the density of the fluid, c the sound velocity, μ_s the shear viscosity, c_p and c_v are the isobaric and isochoric specific heat capacities and ν the thermal conductivity of the fluid. Losses caused by shear and volume viscosity as well as thermal conductivity are summarised in the acoustic loss therm μ. Acoustic absorption in pure fluids has a quadratic frequency dependence ω^2,
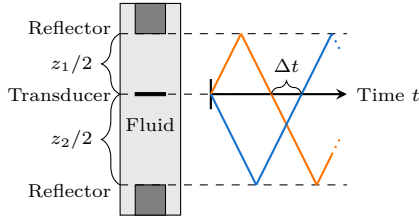
Fig. 1: Schematic of the precision sound velocity measurement set-up [7] with two reflectors and the propagation of acoustic signals over time.

restricting the applicability of Equation 1 to monochromatic acoustic waves. A method to determine acoustic absorption is presented that relies on reference absorption data and experimental signals from high precision speed of sound measurements [7]. The challenge in realizing acoustic absorption measurement lies in separating the effect of absorption in the fluid from diffraction of the ultrasonic wave, the influence of the frequency dependence of the absorption mechanism and the ultrasound transducer's transfer function. While some of these effects can be treated by means of signal processing, others require comparison with reference data. In a fluid-independent calibration approach, a model is devised to describe the systematic measurement deviation correcting the measured acoustic absorption values. The parametrisation of the model is supported by acoustic field simulations, while the identification of the model function is performed using present measurements and reference data. This approach allows for the set-up for precision sound velocity measurement to remain unchanged, while absorption can be determined as a second property using the same signals.

2 Signal processing

While Equation 1 shows how acoustic absorption is related to several properties of the fluid, it also shows that the absorption mechanism depends on the acoustic's wave frequency. Thus, the approach of observing the different signal intensities of the two echoes received when using the measurement set-up as depicted in Figure 1 is only applicable if the acoustic signal is assumed to be monochromatic. While geometric dissipative effects, such as diffraction, are not treated by means of signal processing, the influence of the transducer can be eliminated and the frequency-independent absorption parameter $a = \alpha/\omega^2$ can be determined directly [5]. Since the absorption mechanism is frequency-dependent, the spectrum of the acoustic signal changes during transmission through the medium. The influence on the amplitude spectrum $U(\omega, z) = |U(j\omega, z)|$

can be described by

$$U(\omega, z) = U_0(\omega)e^{-\alpha(\omega)z}, \quad (2)$$

where $U_0(\omega)$ is the spectrum of the signal generated by the transducer [8]. For the presented method $U_0(\omega)$ can be arbitrarily chosen without altering the result. Thus, it may even contain the transfer function of the receiving transducer and the electrical transmission. By putting no restrictions on $U_0(\omega)$, other than to be linear and independent of the distance z the acoustic wave has travelled, the influence of the transducer on the result of the measurement can be eliminated. This is important because the measurements need to be performed over wide temperature and pressure ranges that influence e.g. the transducer's resonance frequency. To find a relation between a frequency-dependent absorption mechanism ($\alpha = a\omega^2$) and the changes in the signal's amplitude spectrum, the zeroth raw moment of $U(\omega, z)$ is evaluated

$$m_0(U(\omega, z)) = \int_{-\infty}^{\infty} U_0(\omega)e^{-a\omega^2 z} \, d\omega. \quad (3)$$

An expression for the change in that raw moment is found by forming the derivative of $m_0(U(\omega, z))$ with respect to z, which then shows the following relation to the second raw moment

$$\partial_z m_0(U(\omega, z)) = \int_{-\infty}^{\infty} -a\omega^2 U_0(\omega)e^{-a\omega^2 z} \, d\omega$$

$$= -a \int_{-\infty}^{\infty} \omega^2 U_0(\omega)e^{-a\omega^2 z} \, d\omega \quad (4)$$

$$= -a \cdot m_2(U(\omega, z)).$$

Consequently, if the derivative of the raw moment of zeroth order and the raw moment of the second order are known, the absorption parameter a can be determined. However, while raw moments of arbitrary order can be calculated straightforwardly from given signals, their derivatives are not trivial. The objective is to evaluate only two signals and consequently $m_0(U(\omega, z))$ is only available at two different distances z. Observations as well as theoretical considerations for Gaussian spectra ($U_0(\omega) = \hat{U} \exp\left(-\left(\frac{\omega - \omega_0}{b}\right)^2\right)$) show that $m_0(U(\omega, z))$ decays exponentially with z, if bandwidth b and absorption parameter a are small ($ab^2 z \ll 1$). Thus, an exponential expression for $m_0(U(\omega, z))$ (e.g. $m_0(U(\omega, z)) = me^{-nz}$) can be assumed. Because $m_0(U(\omega, z))$ can be determined at two spatial positions z_1 and z_2, m and n are calculated by inserting $m_0(U(\omega, z_1))$ and $m_0(U(\omega, z_2))$ at z_1 and

z_2. The resulting expression for $m_0(U(\omega, z))$ can then be derived analytically. After substitution into Equation 4, this yields an expression for the absorption parameter a

$$a = \frac{1}{z_2 - z_1} \frac{m_0(U(\mu(\omega, z_1))}{m_2(U(\omega, z_1))} \ln\left(\frac{m_0(U(\omega, z_1))}{m_0(U(\omega, z_2))}\right). \quad (5)$$

This equation can be used to determine the absorption parameter a directly, without making assumptions about the signal other than assuming its bandwidth to be sufficiently limited. Further aspects of this method can be found in reference [5].

3 Reference data

Some effects that may distort acoustic absorption measurements can be rectified by means of signal processing (see section 2). Others, such as dissipation of acoustic energy caused by diffraction of the acoustic wave and non-ideal reflectors, are modelled as systematic measurement deviation, which can be corrected mathematically. To model this systematic deviation, however, reference data for acoustic absorption are required. It is evident from Equation 1 that several properties of the fluid have to be known for the respective thermodynamic state to calculate acoustic absorption. With the exception of volume viscosity, these proprieties are acquired from the reference database *REFPROP* [16]. For volume viscosity, all data sets for water [2, 3, 9–12, 17–21, 23], methanol [3, 11, 14, 15], toluene [1, 2], and n-hexane [1] are checked for plausibility and consistency. For each fluid, the volume viscosity measurement data are appropriately interpolated. These models are then used in conjunction with *REFPROP* to determine reference data for acoustic absorption for the specific thermodynamic state where the reference measurements are performed at. However, it should be noted that these states differ only slightly from the reference states. Only a limited number of datasets supply information about the uncertainty of the respective measurement, which varies from $< 1\,\%$ [23] to $5\,\%$ [21]. Due to the lack of reliable data, the uncertainty of the reference data is estimated using the error of the interpolation function.

4 Parametrising the systematic measurement deviation

For the systematic measurement deviation to be modelled successfully, first, it has to be shown that the resulting expression is relatively simple from a mathematical standpoint. Even if there are, as in the presented case, multiple
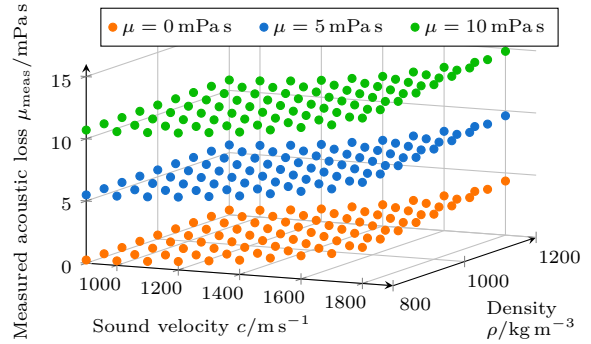

Fig. 2: Acoustic loss determined from simulation signals for different thermodynamic conditions.

reference measurements that can be used to identify a function that models the systematic measurement deviation, a simple function with few parameters is preferred as it is expected to result in a more stable and reliable solution. As an approach to parametrise such a function, acoustic field simulations based on finite differences are performed in *pyfds* [4]. The simulation model is axially symmetric and based on the physical measurement set-up (Figure 1) with the transducer simply described as an infinitely thin disc. For performance reasons, the reflectors are modelled as fluids with the same acoustic impedance as stainless steel to consider the losses occurring due to imperfect reflection. The simulation volume is the same as the inner cell of the measurement set-up and the boundaries are reflecting. The spatial resolution of the simulation is chosen to allow for waves with wavelength λ to propagate without significant numeric distortion ($\Delta r = \Delta z = \lambda/20$). Temporal resolution is chosen to maintain stable simulation conditions at higher sound velocities c ($\Delta r/\Delta t > c$). The resulting simulation model consisted of $12 \cdot 10^6$ spatial points for which the acoustic pressure is calculated over $45 \cdot 10^3$ time steps. One simulation run takes about 50 h.

To parametrise the model for the evaluation of the systematic measurement deviation, the simulations are performed for different sound velocities c, densities ρ and acoustic losses $\mu = \frac{4}{3}\mu_s + \mu_v + \frac{c_p - c_v}{c_p \cdot c_v}\nu$. The range for these parameters to be explored is similar to that of the examined fluids. The resulting signals generated by the simulation are evaluated using the method described in section 2 in conjunction with Equation 1 and its relation to the absorption parameter a ($\mu_{meas} = 2a_{meas}\rho c^3$). The resulting estimates for the acoustic loss are depicted in Figure 2. As is clearly visible, the estimated loss shows the expected deviation from the values of the acoustic loss in the fluid. It is apparent that the observed systematic deviation depends strongly on sound velocity and density. Closer observation reveals that the deviation is also a function of the acoustic loss itself, as can for example be
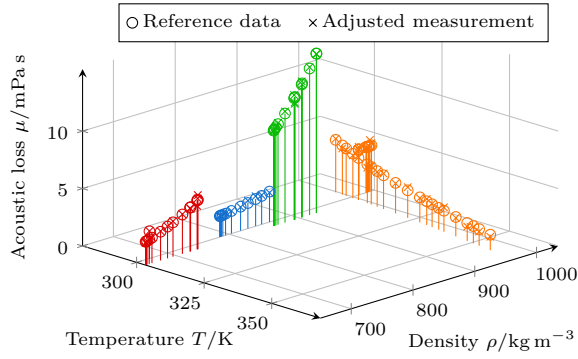
Fig. 3: Acoustic loss reference data (section 3) and adjusted measurement results (Equation 6) for water ($\otimes$), methanol ($\otimes$), toluene ($\otimes$), and n-hexane ($\otimes$).

Fig. 4: Measured volume viscosity and reference data of n-hexane at $303.2\,\mathrm{K}$ and n-octane at $300\,\mathrm{K}$.

observed at a sound velocity of $900\,\mathrm{m\,s^{-1}}$ and a density of $800\,\mathrm{kg\,m^{-3}}$ at the far left of Figure 2. While the deviation for the estimated acoustic loss is close to zero if no absorption is present in the simulated fluid, it increases for higher acoustic losses μ. However, the results show a monotonic trend over the investigated parameters, showing that a model function for the deviation can be assumed to be a rather simple mathematical expression. Therefore, for the modelling of the systematic measurement deviation, polynomials of at most second order in c, ρ and μ_{meas} are used.

5 Results

To identify the systematic measurement deviation for absorption measurement using the physical measurement setup [7], measurements are performed for water, methanol, toluene and n-hexane. Care is taken to assure that the measurements are carried out at thermodynamic states for which reference absorption data exist. 71 reference measurements are used to identify the systematic measurement deviation, with different numbers of measurements for each fluid (30 for water, 12 for methanol, 14 for toluene, 15 for n-hexane), resulting from varying numbers of reference data sets (section 3). Using the results of section 4 as a starting point, the following function with parameters p_i is found to model the systematic measurement deviation caused by the acoustic field with a root mean squared error of $0.185\,\mathrm{mPa\,s}$

$$\mu = p_0 + p_1 c + p_2 c^2 + p_3 \rho + p_4 \rho^2$$
$$+ p_5 \mu_{\mathrm{meas}} + p_6 \mu_{\mathrm{meas}}^2 + p_7 c\rho + p_8 c\mu_{\mathrm{meas}}, \quad (6)$$

with good agreement between reference data and adjusted measurement results (Figure 3). Adding temperature-dependent terms to account for a possible temperature dependence of the system aside form the properties of
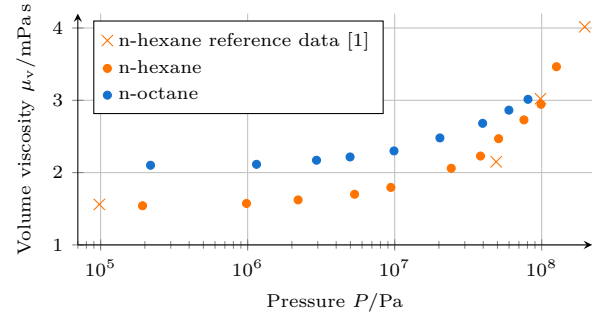
the fluid did not decrease the error of the fit further. This supports the assumption that the signal processing method presented in section 2, along with the modelling of the systematic measurement deviation, allows for an abstraction of the fluid to the properties density ρ, sound velocity c and acoustic loss μ. As a result, the determined model (Equation 6) can be used to adjust the measured acoustic loss μ_{meas} of fluids similar to the reference fluids to compensate for the systematic measurement deviation. If shear viscosity, thermal conductivity and the specific heat capacities are known as well, the volume viscosity can then be determined (Equation 1). As an example, measurement results for n-hexane are presented in Figure 4, showing good agreement with the reference data [1]. To show that the measurement method can be applied to characterise arbitrary fluids, given that they have similar properties to the reference fluids, acoustic loss is measured for n-octane (Table 1). A comparison with the measurement results of the n-hexane measurements show a higher volume viscosity of n-octane (Figure 4) with similar pressure dependence. This behaviour may be explained by the similar molecular structure of both fluids, with the bigger molecule exhibiting increased volume viscosity [1].

The uncertainties of the results are calculated following the *Guide to the Expression of Uncertainty in Measurement* [13]. All uncertainties U_μ are expanded uncertainties with a coverage factor $k = 2$, providing a level of confidence of approximately $95\,\%$ (Table 1). The uncertainty of the measured temperature and pressure (Type B evaluation) and uncertainty of the initial measurements μ_{meas} (Type A evaluation) are taken into account. Uncertainty caused by the model function is estimated by dividing the sum of squared errors of the model (Equation 6) by the degrees of freedom of the modelling approximation [6]. The uncertainty caused by the model of the systematic measurement deviation (Equation 6) as well as the uncertainties of the equations of state [16], used for the calculation of density and sound velocity, are identified as main contributions to the uncertainty U_μ. The estimation of the uncertainty of

Table 1: Acoustic loss, uncertainty of acoustic loss measurement, and derived [16] volume viscosity for n-octane.

Temperat. T/K	Pressure P/MPa	Aco. loss $\mu/\mathrm{mPa\,s}$	Uncertainty $U_\mu/\mathrm{mPa\,s}$	Volume visc. $\mu_\mathrm{v}/\mathrm{mPa\,s}$
300.00	0.2185	2.78	0.26	2.10
299.99	1.1491	2.80	0.27	2.11
299.97	2.9414	2.87	0.27	2.17
299.98	4.9734	2.93	0.27	2.22
299.98	9.8946	3.05	0.29	2.25
299.99	20.3164	3.31	0.32	2.45
299.99	39.6674	3.67	0.38	2.68
299.99	59.8387	4.03	0.46	2.86
299.91	80.6748	4.38	0.53	3.01

the volume viscosity is omitted as it strongly depends on the uncertainty of the shear viscosity, thermal conductivity and heat capacity models (Equation 1).

6 Outlook

The presented method for the determination of acoustic absorption and volume viscosity relies heavily on the existence of reference data. To expand the range regarding the acoustic properties in which measurements can be conducted, existing reference measurements from noble gases, especially liquid xenon, will be included in the modelling calculation. Additionally, reference data generated via molecular dynamics simulation can be used to expand and refine the adjusted measurement results. Further, the authors aim to adapt the measurement set-up to reduce the systematic measurement deviation caused by superimposed dissipative effects and thereby the dependence on reference measurements.

References

[1] J. Allegra, S. Hawley, and G. Holton. Pressure dependence of the ultrasonic absorption in toluene and hexane. *The Journal of the Acoustical Society of America*, 47(1B):144–150, Jan. 1970. 10.1121/1.1911446.

[2] J. R. Allegra and S. A. Hawley. Attenuation of sound in suspensions and emulsions: Theory and experiments. *The Journal of the Acoustical Society of America*, 51(5B):1545–1564, 1972. 10.1121/1.1912999.

[3] O. Awasthi. Temperature dependence of ultrasonic attenuation in associated liquids. *Physics Letters A*, 61(2):122–124, Apr. 1977. 10.1016/0375-9601(77)90857-x.

[4] L. Claes and M. Webersen. pyfds 0.1.2 – modular field simulation tool. 10.5281/zenodo.2649827, Apr. 2019.

[5] L. Claes, S. Johannesmann, E. Baumhögger, and B. Henning. Quantifying frequency dependent absorption phenomena. In *2019 International Congress on Ultrasonics*, 2019.

[6] DAkkS. Bestimmung von Thermometerkennlinien. Technical report, Deutsche Akkreditierungsstelle GmbH, 2010.

[7] F. H. Dubberke, D. B. Rasche, E. Baumhögger, and J. Vrabec. Apparatus for the measurement of the speed of sound of ammonia up to high temperatures and pressures. *Review of Scientific Instruments*, 85(8):084901, 2014.

[8] M. Fink, F. Hottier, and J. F. Cardoso. Ultrasonic signal processing for in vivo attenuation measurement: Short time fourier analysis. *Ultrasonic Imaging*, 5(2):117–135, 1983. ISSN 0161-7346. 10.1177/016173468300500202.

[9] F. E. Fox and G. D. Rock. Compressional viscosity and sound absorption in water at different temperatures. *Phys. Rev.*, 70:68–73, July 1946. 10.1103/PhysRev.70.68.

[10] L. Hall. The origin of ultrasonic absorption in water. *Physical Review*, 73(7):775–781, Apr. 1948. 10.1103/physrev.73.775.

[11] S. Hawley, J. Allegra, and G. Holton. Ultrasonic-absorption and sound-speed data for nine liquids at high pressures. *The Journal of the Acoustical Society of America*, 47(1B):137–143, Jan. 1970. 10.1121/1.1911444.

[12] M. Holmes, N. Parker, and M. Povey. Temperature dependence of bulk viscosity in water using acoustic spectroscopy. *Journal of Physics: Conference Series*, 269(1):012011, 2011.

[13] Joint Committee for Guides in Metrology. Guide to the expression of uncertainty in measurement, 2008.

[14] S. K. Kor, O. N. Awasthi, G. Rai, and S. C. Deorani. Structural absorption of ultrasonic waves in methanol. *Physical Review A*, 3(1):390–393, Jan. 1971. 10.1103/physreva.3.390.

[15] S. K. Kor, S. C. Deorani, and B. K. Singh. Origin of ultrasonic absorption in methanol. *Physical Review A*, 3(5):1780–1783, May 1971. 10.1103/PhysRevA.3.1780.

[16] E. Lemmon, M. Huber, and M. McLinden. REFPROP 9.1. *NIST Standard Reference Database*, 23, 2013.

[17] T. A. Litovitz and E. H. Carnevale. Effect of pressure on sound propagation in water. *Journal of Applied Physics*, 26(7):816–820, 1955. 10.1063/1.1722101.

[18] J. M. M. Pinkerton. A pulse method for the measurement of ultrasonic absorption in liquids: Results for water. *Nature*, 160:128–129, July 1947. 10.1038/160128b0.

[19] J. M. M. Pinkerton. The absorption of ultrasonic waves in liquids and its relation to molecular constitution. *Proceedings of the Physical Society. Section B*, 62(2):129–141, 1949.

[20] J. Rouch, C. C. Lai, and S. H. Chen. Brillouin scattering studies of normal and supercooled water. *The Journal of Chemical Physics*, 65(10):4016–4021, Nov. 1976. 10.1063/1.432853.

[21] M. C. Smith and R. T. Beyer. Ultrasonic absorption in water in the temperature range 0 °C − 80 °C. *The Journal of the Acoustical Society of America*, 20(5):608–610, 1948. 10.1121/1.1906415.

[22] V. Sutilov and P. Hauptmann. *Physik des Ultraschalls: Grundlagen*. Springer Vienna, 2013. ISBN 9783709187500.

[23] J. Xu, X. Ren, W. Gong, R. Dai, and D. Liu. Measurement of the bulk viscosity of liquid by brillouin scattering. *Applied Optics*, 42(33):6704–6709, Nov. 2003. 10.1364/AO.42.006704.