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# Bulk viscosity and compressibility measurement using acoustic spectroscopy

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Bulk viscosity is a somewhat obscure parameter that appears in the hydrodynamic equations for Newtonian liquids when compressibility is important and, together with the dynamic viscosity, controls sound attenuation. Whereas dynamic viscosity reflects only “translational” molecular motion, in contrast the bulk viscosity reflects the relaxation of both “rotational” and “vibrational” degrees of molecular freedom. Several molecular theories yield predictive expressions for both bulk and dynamic viscosities, but experimentally the situation is quite out of balance, in that there is extensive data for the dynamic viscosity of all sorts of liquids, but a paucity of data for bulk viscosity, just a few values for water and a handful of exotic liquids. We compare three possible experimental techniques for measuring bulk viscosity, namely, Brillouin spectroscopy, Laser transient grating spectroscopy, and acoustic spectroscopy. We then formulate some arguments suggesting that acoustic spectroscopy is not only the most suitable for measuring bulk viscosity, but that it also offers a verification procedure that can confirm that the measured parameter agrees with theoretical definition of bulk viscosity for a Newtonian liquid. In addition, acoustic spectroscopy provides a measurement of sound speed, which cannot only improve the attenuation measurement but as a side benefit can also be used to calculate liquid compressibility. We apply this technique for measuring the bulk viscosity and compressibility of twelve commonly assumed Newtonian liquids, two of which surprisingly fails to pass a verification test described here to test the Newtonian hypothesis. Then, we test correlation between measured bulk viscosity and several other intensive properties of these liquids, such as density, dynamic viscosity, dielectric permittivity, and compressibility. We have not discovered any meaningful correlation. This suggests that bulk viscosity is an independent parameter that reflects peculiar properties of liquids and can be used in the set of independent equations describing molecular interaction in liquids. © 2009 American Institute of Physics. [DOI: [10.1063/1.3095471](https://doi.org/10.1063/1.3095471)]

## I. INTRODUCTION

### A. Bulk viscosity as defined in the Navier–Stokes equation

Bulk viscosity appears in a general presentation of the Navier–Stokes equation that can be found in most books on hydrodynamics, for example, Happel and Brenner,<sup>1</sup> Landau and Lifshitz<sup>2</sup> and the fundamental work on theoretical acoustics by Morse and Ingard.<sup>3</sup> For a *compressible* Newtonian liquid this Navier–Stokes equation can be written as

$$\rho \left[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\text{grad } P + \eta \Delta \mathbf{v} + \left( \eta^b + \frac{4}{3} \eta \right) \text{grad div } \mathbf{v}, \quad (1)$$

where  $\rho$  is density,  $t$  is time,  $\mathbf{v}$  is liquid velocity,  $P$  is pressure,  $\eta$  is shear viscosity, and  $\eta^b$  is bulk viscosity. There is some confusion regarding the term “bulk viscosity,” which is referred to as “volume viscosity,” “second viscosity coefficient,” “expansion coefficient of viscosity,” or “coefficient of bulk viscosity” by various authors working in different fields

such as hydrodynamics, acoustics, analytical chemistry, molecular theory of liquids, and rheology. We list some pertinent papers in Appendix A.

The last term on the right hand side of this equation takes into account the compressibility of the liquid and becomes important only for such effects where liquid compressibility cannot be neglected. Otherwise, for an *incompressible* liquid, where

$$\text{div } \mathbf{v} = 0, \quad (2)$$

the Navier–Stokes equation reduces to the much more familiar form given by

$$\rho \left[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\text{grad } P + \eta \Delta \mathbf{v}. \quad (3)$$

If liquid compressibility is unimportant we are then, and only then, justified in using the simpler approximation of Eq. (1). Indeed, many textbooks just assume the liquid to be incompressible and bulk viscosity therefore plays no role. It is not surprising that bulk viscosity is little known when the modern book by Yaws<sup>4</sup> and Ref. 5 do not mention it at all.

Interestingly, it was noted by Stokes, indeed known as “Stokes’s hypothesis,”<sup>6,7</sup> that there are a few compressible fluids, such as monatomic gases, where this bulk viscosity is

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zero. This hypothesis raised some questions about the very existence of bulk viscosity, even in liquids. Several papers<sup>19,20</sup> discuss this issue and take up the task of proving that bulk viscosity does indeed exist for liquids. Experimental justification for the existence of a bulk viscosity for liquids remained elusive with a paucity of meaningful data. Modern measurement techniques now allow precise determination of bulk viscosity as will be shown here. In fact, we found that the bulk viscosity is not even close to zero for any of the liquid that we measured and, in fact, the bulk viscosity is often larger than the dynamic viscosity, as we will show later.

One might ask why one should bother to learn about this seemingly obscure bulk viscosity. A general answer was given by Temkin,<sup>8</sup> who presented a very clear physical interpretation of both dynamic and bulk viscosities in terms of molecular motion. He points out that molecules have “translational,” “rotational,” and “vibrational” degrees of freedom in liquids and gases. The classical dynamic viscosity  $\eta$  is associated only with the translational motion of the molecules. In contrast, the bulk viscosity  $\eta^b$  reflects the relaxation of both rotational and vibrational degrees of freedom. This leads one to conclude that if one wants to study rotational and vibrational molecular effects in complex liquids, one must learn how to measure bulk viscosity.

A more specific answer is that measuring the bulk viscosity, a typical output parameter of molecular theory models, allows one to then test the validity of such models. As one important example, Enskog's theory<sup>9</sup> yields an analytical expression for both dynamic and bulk viscosities.

$$\eta = b_0 \left( \frac{1}{Y} + 0.8 + 0.761 * Y \right), \quad (4)$$

$$\eta^b = 1.002 * b_0^* Y, \quad (5)$$

where  $b_0$  is second virial coefficient and  $Y$  is relative collision frequency.

Another classical theory by Kirkwood and co-workers<sup>10,11</sup> presents integral expressions for both dynamic and bulk viscosities. However, at the end of the paper, they declared that numerical calculation of the integrals is possible only for dynamic viscosity, stating that a numerical procedure for calculating bulk viscosity is not possible due to “...extraordinary sensitivity to the equilibrium radial distribution function....”

There are several recent theories for calculating bulk viscosity for Lennard-Jones liquids using the Green-Kubo model. They are described in theoretical papers by Hoheisel *et al.*,<sup>12</sup> Okumura and Yonezawa,<sup>13,14</sup> Meier,<sup>15</sup> Dyer *et al.*,<sup>16</sup> and Bertolini and Tani.<sup>17</sup>

Verification of these theories requires experimental data for the bulk viscosity of Newtonian liquids, but strangely enough there are only a few studies known to us that report experimental bulk viscosities for such Newtonian liquids. The first is a fifty year old review by Litovitz and Davis<sup>18</sup> that reports a bulk viscosity for water of 3.09 cP at 15 °C and for methanol 2.1 cP at 2 °C. This reported value for the bulk viscosity for water can serve as a reference point for new studies on this subject and validate the applied experi-

mental procedure. It is noted that this review also present bulk viscosity values for molten salts, molten metals, and some other exotic liquids at very low temperatures, but this is not particularly helpful data in the current context..

The second more recent study by Malbrunot *et al.*<sup>19</sup> presents bulk viscosity data for liquid argon, krypton, and xenon near their triple point. This article includes a very clear account of the experimental technique and we will follow a similar procedure, with some additional steps that provide better precision. There are also some reports of the bulk viscosity in liquid metals, such as by Jarzynski.<sup>41</sup>

This paucity of bulk viscosity data is surprising as expressed by both Temkin<sup>8</sup> in his book, as well as Graves and Argow in their paper.<sup>20</sup> The main goal of this paper is to add more experimental data for the bulk viscosity of Newtonian liquids and to formulate procedures that can be easily reproduced by other scientists with commercially available instruments.

## B. Calculation of bulk viscosity from attenuation

To date, measurement of ultrasound attenuation is the only known way of experimentally studying bulk viscosity.<sup>19</sup> Viscosity and thermal conduction are the two mechanisms that cause attenuation when ultrasound propagates through a homogeneous media and modern theory<sup>3,7,8</sup> takes both of these into account.

Thermal conduction contribution is proportional to the deviation of the ratio of specific heats ( $\gamma$ ) from unity for a particular fluid, ( $\gamma-1$ ). The value of specific heat ratio for most liquids is very close to 1 due to low compressibility, in contrast with gases where this parameter may substantially exceed 1. Therefore, the thermal conduction contribution to the ultrasound attenuation in liquids is usually negligible. Consequently, ultrasound attenuation in liquids depends mostly on viscosity related effects, which is to say it is rheological in nature. The same assumption has been used in previous studies<sup>19</sup> on this subject.

The solution of the general Navier-Stokes equation [Eq. (1)] with regard to attenuation of a plane, one-dimensional wave while propagating through a viscous thermally nonconductive liquid, is given in many books on acoustics.<sup>7,8</sup> This solution yields the following expression for the ultrasound attenuation coefficient  $\alpha_{\text{long}}$ :

$$2 \left( \frac{\alpha_{\text{long}} V}{\omega} \right)^2 = \frac{1}{\sqrt{1 + \omega^2 \tau_v^2}} - \frac{1}{1 + \omega^2 \tau_v^2}, \quad (6)$$

where,  $V$  is sound speed,  $\omega$  is ultrasound frequency,  $\tau_v$  is viscous relaxation time that takes into account both the bulk viscosity and the shear viscosity as given by

$$\tau_v = \frac{1}{\rho V^2} \left( \frac{4}{3} \eta + \eta^b \right). \quad (7)$$

This viscous relaxation time is very short, of the order of  $10^{-12}$  s.

Attenuation as a function of frequency is a bell-shaped curve. It reaches maximum value at a so-called critical frequency that corresponds to the wave period, which is approximately equal to the viscous relaxation time. For the

TABLE I. Literature data on viscosity, dielectric permittivity, and density of the 12 Newtonian liquids.

Liquid name	Description	Supplier	At 25 °C			
			Viscosity (cP)	Density (g/cm <sup>3</sup> )	Dielectric constant	Compressibility × 10 <sup>10</sup> /Pa
Cyclohexane C <sub>6</sub> H <sub>12</sub>	>99%, ACS reagent	Sigma-Aldrich	0.894	0.778	2.02	1.13 at 20 °C
Cyclohexanone	>99.5%	Fluka	2.017	0.948	16.10	
1-pentanol	>98%	Fluka	3.619	0.811	13.90	0.771 at 0 °C
Toluene	>99.5%, ACS reagent	Sigma-Aldrich	0.560	0.897	2.38	0.896 at 20 °C
Methanol	>99%, spectrophotometgrade	Sigma	0.544	0.791	33.00	1.21 at 20 °C
Hexane	>95% reagent grade	Sigma-Aldrich	0.300	0.660	1.89	1.669
2-propanol	>99.5% ACS reagent	Sigma-Aldrich	2.040	0.790	20.18	1.33 at 40 °C
Butyl acetate C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	99.5%, urethane grade	Sigma-Aldrich	0.685	0.882	5.07	
Acetone	>99.5%, ACS reagent	Sigma-Aldrich	0.306	0.792 at 20 °C	21.01	1.262 at 20 °C
Ethanol	>99.5%, absolute, 200 proof	Sigma-Aldrich	1.074	0.785	25.30	1.119 at 20 °C
Pyridine	>99%, reagentPlus	Sigma-Aldrich	0.879	0.982	13.26	
Water	distilled	Local pharmacy	0.890	0.997	80.10	0.4524

Newtonian liquids, this critical frequency is about 1000 GHz due to the very short viscous relaxation time. It is extremely hard to achieve such high ultrasound frequencies in real instruments, but, fortunately, the low frequency asymptotic function of Eq. (6) is quite adequate for interpreting the acoustic data. This asymptotic function is given by

$$\alpha_{\text{long}} = \frac{\omega^2}{2\rho V^3} \left[ \frac{4}{3} \eta + \eta^b \right]. \quad (8)$$

This expression for ultrasound attenuation is closely related to the “Stokes’ law for sound attenuation”<sup>6</sup> derived 160 years ago by the same famous Stokes who derived the well known expression for the frictional drag on a particle moving in a viscous liquid. He used the Navier–Stokes equation for an incompressible liquid [Eq. (3)], which yields the following simplified equation for sound attenuation  $\alpha_{\text{long}}$  for Newtonian liquid:

$$\alpha_{\text{long}} = \frac{2\omega^2 \eta}{3\rho V^3}. \quad (9)$$

Stokes’ presentation neglects liquid compressibility and consequently the bulk viscosity term is missing. The attenuation predicted by Stokes’ is often referred to as “classical.”

Instead of Stokes’ law, the more general Eq. (8) serves as a theoretical basis for calculating the bulk viscosity from the measured attenuation and sound speed. All other parameters in this equation, including the dynamic viscosity, are assumed to be known from independent measurements, or perhaps from Ref. 5.

### C. Verification of Newtonian behavior

A valid application of Eq. (8) for calculating the bulk viscosity of a particular liquid requires that this bulk viscosity is independent of the ultrasound frequency, since this independence is assumed in the derivation of Eq. (6) from the Navier–Stokes equation [Eq. (1)]. This independence of the bulk viscosity with frequency is companion to a somewhat analogous requirement that the dynamic viscosity of a Newtonian liquid is independent of shear rate. A bulk viscosity that is dependent on ultrasound frequency or a dynamic vis-

cosity that is dependent on shear rate each indicates that a given liquid is non-Newtonian over the given frequency or shear rate range, respectively. Appendix B presents more details on the relationship between shear and longitudinal rheologies of Newtonian and non-Newtonian liquids. There is a general notion of longitudinal viscosity  $\eta_{\text{long}}$ , which determines dissipation due to longitudinal stress in non-Newtonian liquid,

$$\eta_{\text{long}} = \frac{2\alpha_{\text{long}}\rho V^3}{\omega^2}. \quad (10)$$

For Newtonian liquid longitudinal viscosity equals sum of bulk viscosity and four-thirds of the dynamic viscosity, both of them are presumably frequency independent,

$$\eta_{\text{long}}(\text{Newtonian}) = \eta^b + \frac{4}{3}\eta. \quad (11)$$

Verification of this frequency independence of the calculated bulk viscosity is essential for subsequent testing of various molecular theories of liquids as mentioned above, which all assume that the liquid obeys the Navier–Stokes equation and is Newtonian from the rheological viewpoint.

This analysis points toward the necessity of making multifrequency measurements of ultrasound attenuation. Such measurement would allow verification of the frequency dependence predicted by Eq. (8), which leads to independence of longitudinal viscosity of frequency. Only if the experiment would match this theoretically predicted frequency dependence and longitudinal viscosity calculated according to Eq. (10) would be constant one could claim bulk viscosity for this particular liquid.

Deviation of the measured attenuation frequency dependence from theoretical one would indicate that there is an additional mechanism of ultrasound attenuation for a particular liquid in addition to the viscous dissipation. For instance, there is a body of literature overviewed by Kaatz<sup>21</sup> describing the application of this extra attenuation for characterizing chemical reactions in liquids. If we did not have this frequency dependence test, we might attribute attenuation coming from chemical reactions to bulk viscosity, which would lead to quite erroneous values for the bulk viscosity value.



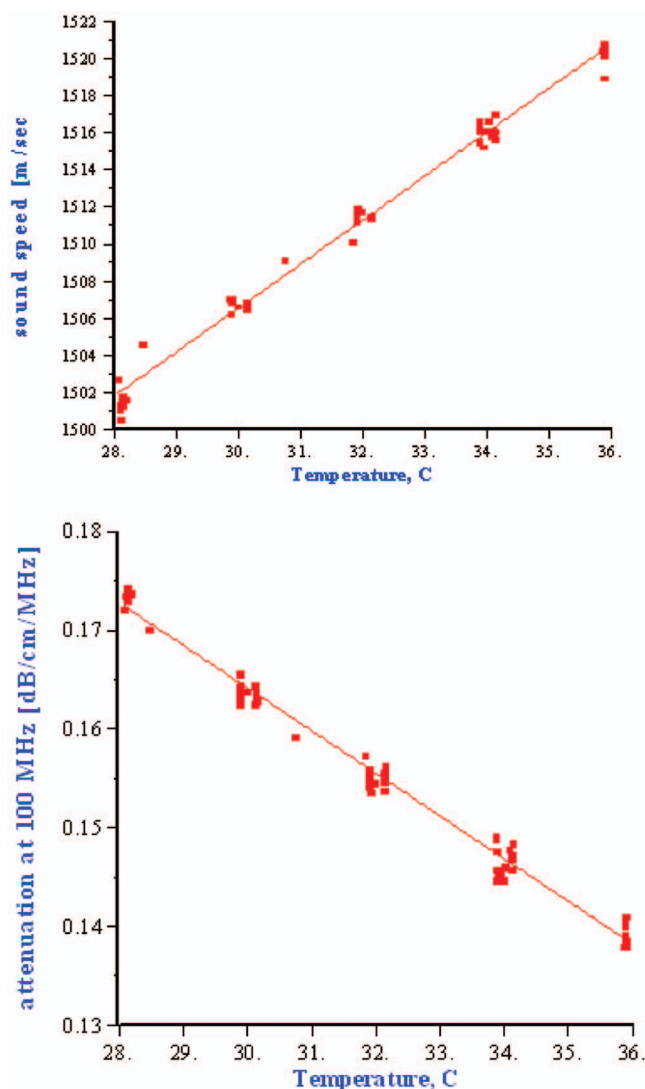


FIG. 1. (Color) Attenuation at 100 MHz and sound speed at 10 MHz of water at different temperatures.

Unfortunately, verification of the attenuation frequency dependence does not yield additional information for confirmation of the assumption that thermal conductance contribution is negligible. Frequency dependence of the thermal conductance contribution to the attenuation is the same for the viscous one. It is still necessary to rely on the small value of the parameter  $(\gamma-1)$  for liquids, as stated above.

## II. MEASUREMENT TECHNIQUES AND INSTRUMENTS

There are at least three different methods of measuring attenuation coefficient that have been applied for characterizing liquids: Brillouin spectroscopy,<sup>22,23</sup> laser transient grating spectroscopy,<sup>24–26</sup> and acoustic spectroscopy.<sup>19,27</sup> Each of these has advantages and disadvantages with regard to this particular task.

The first two methods are usually performed at gigahertz frequencies, whereas acoustic spectroscopy is typically employed in the megahertz range. This difference in frequency ranges makes these techniques complimentary for studying processes with widely different relaxation times.

However, characterizing bulk viscosity measurements at very high frequency might present a serious problem. The attenuation increases rapidly with increasing frequency according to Eq. (8). This means that Brillouin and laser transient grating spectroscopies must deal with much higher attenuations than acoustic spectroscopy. This would present no problem for liquids, such as water, that have little attenuation, but might be a serious problem for many others liquids. For instance, according to our data presented below, the attenuation rate for pyridine is 39 000 dB/cm at 1 GHz. Measurement of that high attenuation would require either very high power excitation, which might generate nonlinear effects, or require measurement over very short distances. Acoustic spectroscopy is clearly preferable for such high attenuating liquids.

Another problem related to Brillouin and Laser transient grating spectroscopies is that these techniques usually report variation in attenuation with temperature, but not frequency. Measurement is usually performed at a single frequency. We stated above that frequency dependence is very useful for validating that the measured attenuation can in fact be used to calculate a meaningful bulk viscosity.

Acoustic spectroscopy, on the other hand, allows simple attenuation measurement at multiple frequencies within frequency range from 1 to 100 MHz. This is yet another argument for using acoustic spectroscopy for characterizing bulk viscosity.

A final argument in favor of acoustic spectroscopy is precision. Malbrunot *et al.*<sup>19</sup> compared the error of Brillouin and acoustic spectroscopies and concluded that acoustic spectroscopy with a precision of just 2.5% is considerably more precise. Modern acoustic spectrometers can improve this error by almost an order of magnitude, as discussed below. Furthermore, error analysis of Brillouin spectroscopy presented by Papayonou *et al.*<sup>22</sup> confirms potentially high errors due to the difficulty in estimating Brillouin linewidth. There is also a problem with regard to laser transient grating spectroscopy. Calculation of the attenuation from the raw data requires fitting with five adjustable parameters, according to Cao *et al.*<sup>24</sup> This makes this method substantially more complicated compared to acoustic spectroscopy, where the attenuation coefficient is measured directly.

This short comparative analysis leads us to conclude that acoustic spectroscopy is more suitable for measuring bulk viscosity, which agrees with a similar analysis by Malbrunot *et al.*<sup>19</sup> Several commercial instruments have been developed during the last decade based on acoustic spectroscopy. These include the Ultrasizer by Malvern Ltd., an instrument from Ultrasonic Scientific, the Acoustosizer by Colloidal Dynamics, Inc., the APS-100 by Matec Applied Sciences Inc., and the DT-100 and DT-600 by Dispersion Technology Inc.

In this study we use a DT-600, which is specifically designed for characterization of longitudinal rheological properties.<sup>27</sup> The DT600 is similar to the instrument used by Malbrunot *et al.*<sup>19</sup> but with several modifications that significantly improve precision. Both instruments are based on the “transmission” principle. However, instead of a “pulse-echo” method with a single transducer, we use two transducers. One functions as transmitter, the other as receiver. The trans-

TABLE II. Attenuation and sound speed of water at two temperatures during multiple temperature sweeps.

Temperature (°C)	Attenuation at 100 MHz (dB/cm MHz)	Sound speed (m/s)	Temperature (°C)	Attenuation at 100 MHz (dB/cm MHz)	Sound speed (m/s)
35.90	0.1385	1520.6	28.13	0.1738	1501.3
35.89	0.1390	1520.4	28.12	0.1732	1500.5
35.89	0.1400	1520.8	28.12	0.1729	1501.3
35.90	0.1379	1520.1	28.13	0.1738	1501.2
35.89	0.1408	1518.9	28.13	0.1742	1501.5
35.90	0.1409	1520.3	28.13	0.1740	1501.8
35.89	0.1404	1520.1	28.19	0.1737	1501.6
35.88	0.1379	1520.4	28.09	0.1734	1501.0
35.89	0.1399	1520.8	28.07	0.1720	1502.7
Average	0.1395	1520.30		0.1734	1501.4
Av. abs. dev.	0.00098	0.35		0.00048	0.39
Precision (%)	0.7	0.02		0.3	0.03

mitting piezoelectric transducer converts an input electrical tone burst to an ultrasound pulse of a certain frequency and intensity  $I_{\text{in}}$  and launches it into the sample. The intensity of this pulse decays as it passes through the sample due to the interaction with the liquid. A second piezoelectric transducer converts this weakened acoustic pulse with intensity  $I_{\text{out}}$  back to an electric pulse and sends it to the electronics for comparison with the initial input pulse.

The distance between transmitter and receiver changes in steps in a manner similar to that described by Malbrunot *et al.*<sup>19</sup> However, instead of only two gaps, our sensor works with 21 gaps, typically from 0.3 to 20 mm, which significantly improves precision. Another difference is that instead of operating at a single frequency, the DT600 operates at multiple frequencies, typically 18 frequencies spaced logarithmically from 3 to 100 MHz. The number of transmitted pulses is automatically adjusted to obtain a specified signal-to-noise ratio, which also contributes to the higher precision. It is convenient to present these raw data in terms of an attenuation coefficient  $\alpha_{\text{exp}}$  defined as

$$\alpha_{\text{exp}}[\text{dB/cm MHz}] = \frac{10}{f[\text{MHz}]L[\text{cm}]} \log \frac{I_{\text{in}}}{I_{\text{out}}}, \quad (12)$$

where  $f$  is the frequency of the pulse and  $L$  is the distance between transmitter and receiver.

The attenuation coefficient  $\alpha_{\text{exp}}$  is the same as defined initially in Eq. (8), but in different units. Decibel units are more widely accepted in Acoustics than *neper*s. Normalization by frequency is useful because the attenuation coefficient varies strongly with the frequency. This normalization allows better graphical presentation of this parameter over a wide frequency range.

The DT600 precision in attenuation measurement is specified as 0.01 dB/cm MHz for all frequencies, but actually improves over this somewhat with increasing frequency. We performed a special test for determining the precision of both attenuation and sound speed measurement and these results are discussed later.

The attenuation measurement is closely linked to the sound speed measurement. One needs to know the sound speed to determine the proper time to sample the delayed

pulse. The DTI acoustic sensor measures sound speed using a time of flight method. The instrument measures the delay time between the transmitted and received pulse for a set of gaps and the sound speed is calculated from a linear regression of this delay versus distance, usually at a single frequency. Measurement of a single attenuation frequency spectra and sound speed takes about five minutes.

The instrument is equipped with temperature measurement and temperature control. This allows measurement at a fixed temperature above ambient maintained with precision 0.1 C. Precise temperature control requires the sample to be adequately mixed during measurement and this normally requires a sample volume of 100 ml, although the sample volume can be as small as 15 ml for samples that do not require stirring and precise temperature control.

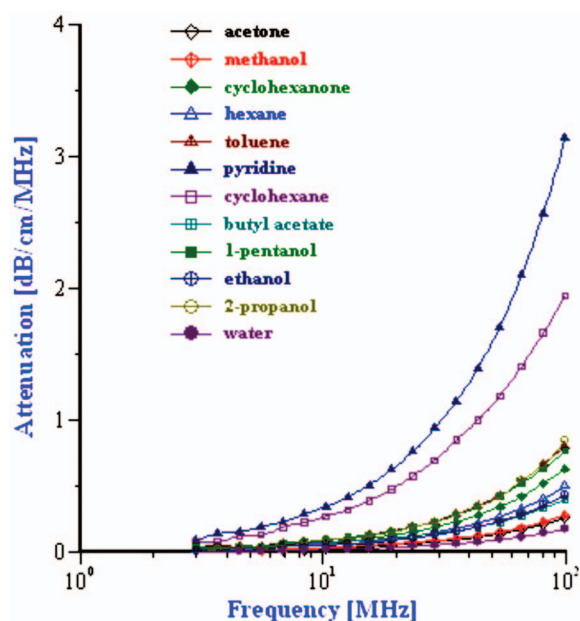


FIG. 2. (Color) Attenuation frequency dependences of 12 different Newtonian liquids. Frequency axis is logarithmic for more even presentation over a wide frequency range.

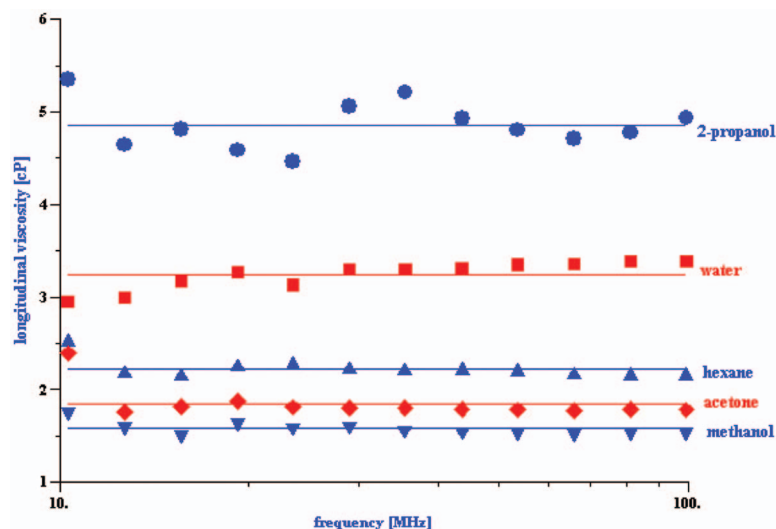


FIG. 3. (Color) Longitudinal viscosity of five Newtonian liquids having a low viscosity.

### III. MATERIALS

We use 12 presumably Newtonian liquids as listed in Table I. We selected these particular liquids based on the availability of independent information regarding dynamic viscosity, density, dielectric permittivity, and compressibility from literature, including Ref. 5. The fact that the authors of this well respected publication found it possible to assign a single value for viscosity at a given temperature indicates that they treat these as Newtonian liquids.

### IV. EXPERIMENTAL PROTOCOL

The attenuation frequency spectra, sound speed, and all other parameters of interest are temperature dependent. Instead of performing measurement at a single fixed temperature, we made measurements at several different temperatures using built-in temperature control. Water was measured in two degree steps from 28 to 36 °C. At least five measurements were made at each temperature. All other liquids were measured at least five times at two different temperatures over a temperature range of no more than 5 °C.

All collected data were fitted with linear temperature regressions. We assumed that attenuation at 100 MHz and sound speed at 10 MHz are linear functions of temperature around 25 °C,

$$\alpha_{100}(T) = \alpha_{100} + \alpha^T(T - 25), \quad (13)$$

$$V(T) = V + V^T(T - 25). \quad (14)$$

This approach not only allows us to determine measured and calculated parameters at room temperature of 25 °C, but also to make linear temperature corrections.

In order to verify this assumed linear temperature dependence, we measured water at five different temperatures over five temperature sweeps. Stirring of the samples is very important to maintain temperature control. The results are shown in Fig. 1. They clearly confirm that attenuation and sound speed vary in a linear manner within this small temperature interval.

This water test yields sufficient data for determining the precision of the attenuation and sound speed measurements

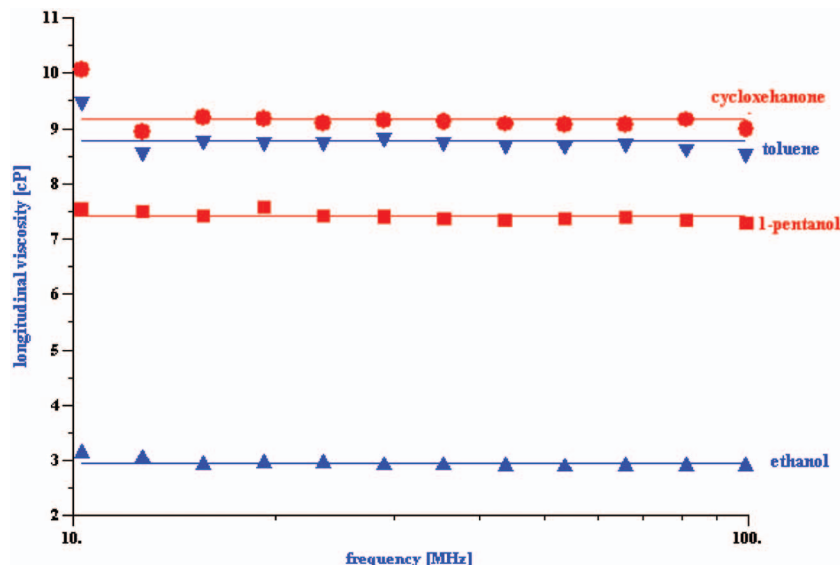


FIG. 4. (Color) Longitudinal viscosity of four Newtonian liquids having a moderate viscosity.

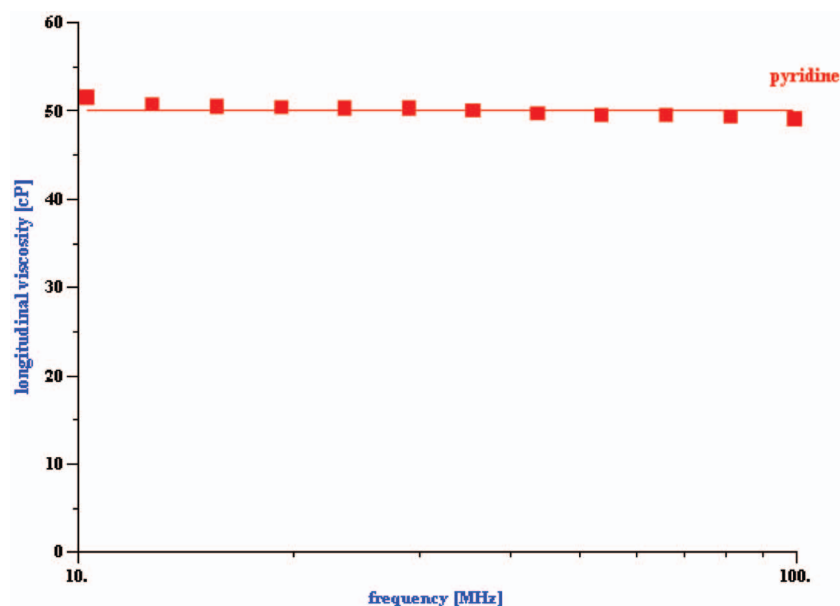


FIG. 5. (Color) Longitudinal viscosity of pyridine having a very high viscosity value.

as discussed below. Calculation of the bulk viscosity from the measured attenuation at 100 MHz has been performed using Eq. (8).

## V. RESULTS AND DISCUSSION

We present results of this study in the following four sections: precision, frequency dependence test, bulk viscosity, compressibility, and correlation between various parameters of the liquids.

### A. Precision

We use water for determining the precision of the attenuation data at 100 MHz and the precision of the sound speed precision at 10 MHz. Figure 1 presents the results of these measurements at different temperatures. Table II presents numerical data for the highest and lowest temperatures. These numbers allow us to calculate precision, which we determine as a ratio of “average absolute deviation” to the “arithmetic

average” value. On this basis, the precision of the attenuation measurement is 0.7% at 35 °C and 0.3% at 28 °C. This is much better than in the older experiments by Malbrunot *et al.*<sup>19</sup> The precision of the sound speed measurement is about 0.03%.

### B. Frequency dependence test

We measured 476 acoustic spectra, together with sound speed, for these 12 liquids. Representative attenuation spectra for all 12 liquids are shown in Fig. 2. We can convert these attenuation spectra to longitudinal viscosity using Eq. (10). For a Newtonian liquid, the longitudinal viscosity, as already noted in Eq. (11), equals the sum of the bulk viscosity and four-thirds the dynamic viscosity and must be frequency independent, which is the essence of the test that we suggest for verifying the Newtonian nature of the liquid.

The calculated longitudinal viscosity differs significantly for these different fluids and is therefore plotted in Figs. 3–6, which separate the liquids into groups according to whether

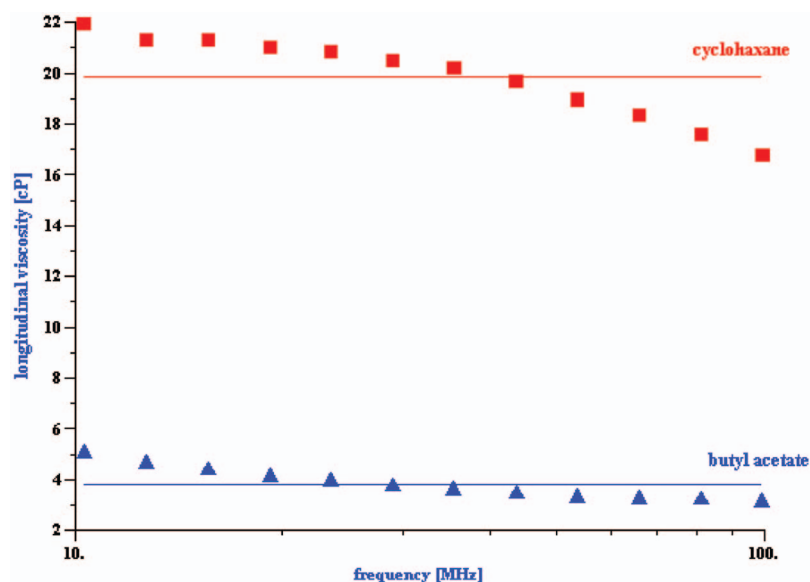


FIG. 6. (Color) Longitudinal viscosity of cyclohexane and butyl acetate as examples of non-Newtonian liquids.



TABLE III. Attenuation at 100 MHz, temperature coefficient, and dynamic and bulk viscosities for 12 liquids.

Liquid name	At 25 °C				
	Attenuation at 100 MHz (dB/cm MHz)	Attenuation $T$ coefficient $\alpha^T$	Dynamic viscosity (cP)	Bulk viscosity (cP)	Linear variation coefficient
Cyclohexane	2.07	−0.05	0.894	“17.4”	“0.082”
Cyclohexanone	0.63	<0.01	2.017	7.0	0.012
1-pentanol	0.79	−0.007	3.619	2.8	0.009
Toluene	0.72	0.009	0.560	7.6	0.014
Methanol	0.26	<0.01	0.544	0.8	0.024
Hexane	0.60	−0.015	0.300	2.4	0.022
2-propanol	0.80	−0.008	2.040	2.7	0.001
Butyl acetate	0.38	0.004	0.685	“2.4”	“0.137”
Acetone	0.25	<0.01	0.306	1.4	0.038
Ethanol	0.42	<0.01	1.074	1.4	0.015
Pyridine	3.90	<0.01	0.879	62.4	0.012
Water	0.186	−0.0043	0.890	2.4	0.036

the calculated bulk viscosity is low, medium, or high and whether the liquid is judged Newtonian or not. On each graph, the points are the experimental data for a given liquid and the lines correspond to the arithmetic average viscosity for that liquid.

Deviation of the experimental data for a particular liquid from its average value is a measure of its Newtonian behavior. It would be convenient to have a measure of how much the longitudinal viscosity deviates from what we would expect for Newtonian fluid. There are multiple ways of introducing such statistically justified measure. We can select the most appropriate one using calculated values of the bulk viscosity shown on Figs. 3–6. The first feature of these figures that catches eye is that two liquids, cyclohexane and butyl acetate, exhibit regular frequency dependence. This is an indication that these liquids are non-Newtonian at this frequency range. The second argument that can be used is an obvious fact that water is a Newtonian liquid.

It turns out that linear variation coefficient reflects these peculiarities the best. This parameter is standard deviation between the linear frequency fit to the experimental data and

average attenuation, normalized with the average attenuation. Table III presents value of this parameter for all liquids in the last column. It is seen that it is much larger for the mentioned above two non-Newtonian liquids comparing to all others. We can suggest to use linear variation coefficient equals to 0.05 as a threshold that separates Newtonian and non-Newtonian liquids, according to this test based on the bulk viscosity.

It is interesting to mention that cyclohexane and butyl acetate are examples of liquids that are judged Newtonian from the viewpoint of only shear viscosity, which nevertheless are judged non-Newtonian when viewed more comprehensively in the light of longitudinal rheology at high frequency. It is perhaps also to interject yet a note of caution.

### C. Bulk viscosity

As mentioned above, the attenuation measured at 100 MHz provides the most precise attenuation measurement.

TABLE IV. Sound speed, sound speed temperature coef, storage modulus, and compressibility for 12 liquids.

Liquid name	At 25 °C			
	Sound speed (m/s)	Sound speed $T$ coef (m/s °C)	Storage modulus ( $G'_{\text{long}} \times 10^9$ Pa)	Compressibility $\times 10^{10}$ /Pa
Cyclohexane	1256	−6.66	1.23	1.15
Cyclohexanone	1407	−4.20	1.88	0.75
1-pentanol	1273	−2.88	1.31	1.07
Toluene	1308	−4.70	1.53	0.92
Methanol	1106	−3.65	0.97	1.46
Hexane	1078	−4.65	0.77	1.84
2-propanol	1143	−4.40	1.03	1.37
Butyl acetate	1193	−4.44	1.26	1.12
Acetone	1166	−4.97	1.08	1.31
Ethanol	1147	−4.26	1.03	1.36
Pyridine	1417	−4.57	1.98	0.72
Water	1496	+2.40	2.23	0.63

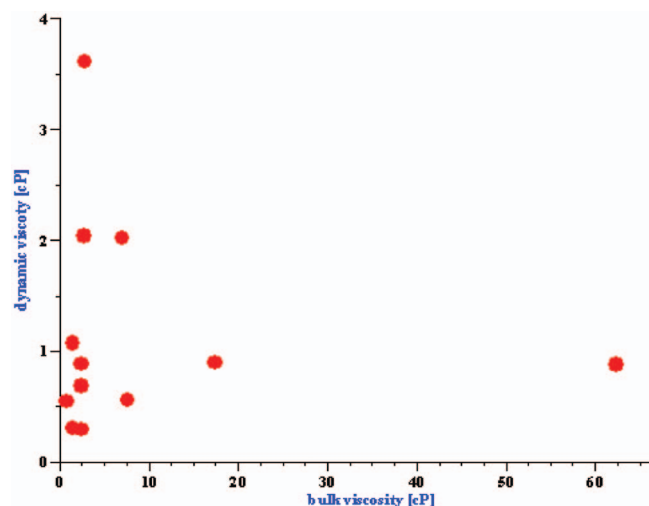


FIG. 7. (Color) Graph illustrating correlation between dynamic viscosity and bulk viscosity.

Table III presents the 100 MHz attenuation at 25 °C for all 12 liquids. Using Eq. (8) we then calculate the bulk viscosity, which is also presented in Table III.

To verify the procedure used here, it would be useful to compare these bulk viscosities with literature values, however, we have independent data only for water from the Litovitz–Davis review.<sup>18</sup> They report a value of 3.09 cP at 15 °C, whereas we obtained a somewhat smaller value of 2.43 cP at a somewhat higher temperature of 25 °C. An even better verification would be to compare the ratio of bulk to shear viscosity at a given temperature. Litovitz–Davis report a ratio of 2.81 at 15 °C, whereas we obtained a value of 2.73 at 25 °C. This is the only room temperature independent verification of our bulk viscosity measurement that we managed to find.

It is interesting to note that the bulk viscosity for these twelve liquids varies over a much wider range than the dynamic viscosity, by almost an order of magnitude. This seems to confirm that the bulk viscosity is more sensitive to the molecular structure of the liquid.

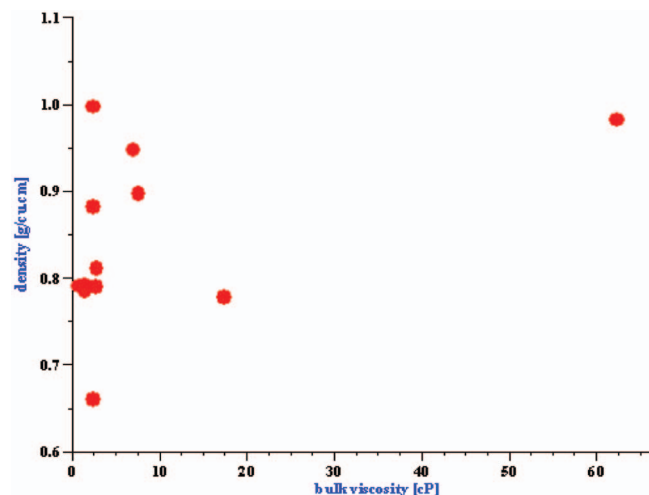


FIG. 8. (Color) Graph illustrating correlation between density and bulk viscosity.

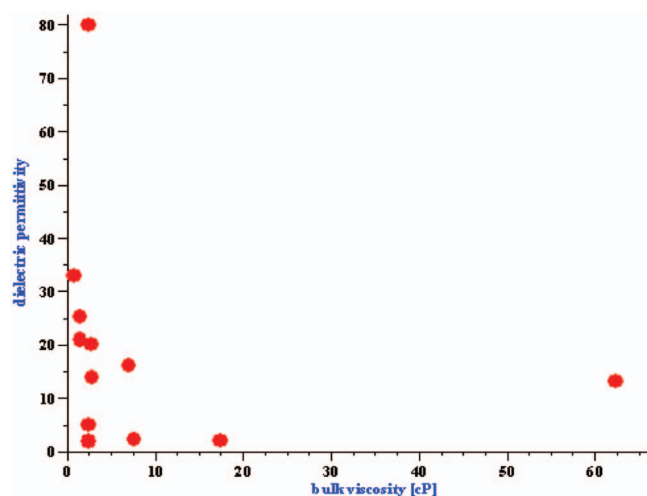


FIG. 9. (Color) Graph illustrating correlation between dielectric permittivity and bulk viscosity.

#### D. Storage modulus and compressibility

Precise sound speed measurement provided by acoustic spectroscopy allows fast, nondestructive, and precise calculation of both storage modulus and compressibility as presented in Table IV for all 12 liquids. These values agree well with independent data from Ref. 5 for some of the liquids. There are some discrepancies for water and the alcohols for yet unknown reasons.

Compressibility is a measure of the liquid elasticity. It is interesting to test the possibility of correlation between elastic and viscous properties of liquids, which is done in the next section.

#### E. Correlation between various intensive parameters of the liquids

Figures 7–10 illustrate the relationship between the bulk viscosity and four other intensive parameters of the liquids presented in the Tables I and III. The wide range of observed bulk viscosity is largely due to one exceptional fluid, namely, pyridine, with a quite unexplained bulk viscosity of 62 cP.

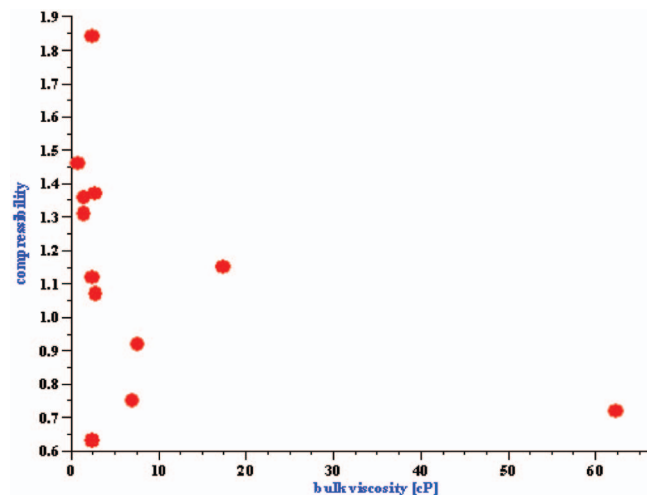


FIG. 10. (Color) Graph illustrating correlation between compressibility and bulk viscosity.

However, even if we remove the peculiar pyridine result, there is no strong correlation between bulk viscosity and other intensive parameters. This seems to confirm that the bulk viscosity is a quite independent parameter, which reflects particular properties of liquids, and can be used as such in the set of equations for studying molecular interactions in liquids.

## VI. CONCLUSIONS

We compared the three known methods for determining the bulk viscosity of liquids and conclude that, typically, acoustic spectroscopy is the best choice because it offers high precision without requiring knowledge of many other liquid properties. Acoustic spectroscopy provides a direct measurement of the attenuation and sound speed of the liquid, which then allows calculation of the bulk viscosity from the attenuation as well as compressibility from the sound speed.

We characterized 12 supposedly Newtonian liquids and report values of the bulk viscosity and compressibility for each. The observed precision of about 0.5% for attenuation and 0.05% for sound speed is sufficient to demonstrate that each of these liquids has a bulk viscosity that is not just comparable with its dynamic viscosity, but in some cases is significantly larger.

Interestingly, the bulk viscosity of these liquids varied over more than a 3:1 range. However, taking these 12 liquids as a set, we see practically no correlation between the bulk viscosity and either dynamic viscosity, dielectric permittivity, density, or compressibility, which offers some confirmation that the bulk viscosity might be treated as an independent parameter in testing various molecular theories of liquids. The measured sound speed and corresponding calculated values of the compressibility is also important for verification of molecular theories of liquids.

Acoustic spectroscopy has an important advantage of providing the frequency dependence of the measured ultrasound attenuation. These spectra allow us to verify whether the calculated bulk viscosity is frequency independent, which is a necessary condition for claiming that the liquid is Newtonian, which in turn is a necessary condition for claiming that the calculated bulk viscosity actually corresponds to the definition of this parameter as a coefficient in the Navier-Stokes equation. We formulated a statistically justified criterion that is based on a comparison of the experimentally measured frequency dependence with the theoretically predicted one in the frequency range from 10 to 100 MHz. Of the 12 presumably Newtonian liquids, only two, cyclohexane and butyl acetate, fail to meet this criterion, which then implies that the reported bulk viscosity is not the truly bulk viscosity of these liquids. Without this test both these liquids would be presumed Newtonian, any calculated bulk viscosity would be incorrect, and any interpretation or verification of molecular theory for them would be confusing at best.

## APPENDIX A: OTHER NAMES FOR “BULK VISCOSITY” IN DIFFERENT SCIENTIFIC DISCIPLINES

We use term “bulk viscosity” throughout this study, but this same property has been referred to by many different names in various scientific disciplines as described below: a rose by any other name.

### 1. In hydrodynamics

The earliest known mention of this parameter was made by Sir Horace Lamb in his famous work in Ref. 28. The sixth edition of this book contains reference to a “*second viscosity coefficient*.” Other more modern books on hydrodynamics by Happel and Brenner,<sup>1</sup> Landau and Lifshitz,<sup>2</sup> as well as Hirschfelder *et al.*,<sup>29</sup> use the same name.

### 2. In acoustics

Theoretical acoustics by Morse and Ingard<sup>3</sup> refers to this parameter as bulk viscosity and we follow here their lead. This same name is used by Kinsler *et al.* in Ref. 7. However, at the same time, Temkin in Ref. 8 uses instead the term “*expansion coefficient of viscosity*.” To obfuscate things a bit further, Litovitz and Davis<sup>18</sup> use yet another term “*volume viscosity*.”

### 3. In analytical chemistry

Kaatze,<sup>21</sup> in an extensive review on ultrasonic spectroscopy for characterizing the chemistry of liquids, uses again the term volume viscosity as did Carroll and Patterson<sup>23</sup> in their study using Brillouin spectroscopy.

### 4. In molecular theory of liquids

Several authors calculate this parameter using various molecular theory of liquids<sup>10–17,30</sup> and following the lead of Morse and Ingard universally adopted the term bulk viscosity.

### 5. In rheology

Hurtado-Laguna and Aleman,<sup>31</sup> in their studies of molten polymers, so far the most important application associated with volume viscosity, again adopted the term volume viscosity. There is also a historical paper by Graves and Argow<sup>20</sup> that applies the term “*coefficient of bulk viscosity*.”

## APPENDIX B: LONGITUDINAL RHEOLOGY AND SHEAR RHEOLOGY

As noted in rheological handbooks, there are two distinctively different types of rheology: “shear rheology” and “extensional rheology” (Barnes<sup>32</sup>). Basically, they differ in the geometry of the applied stress. In shear rheology the stress is tangential to the surface from which the stress is applied. This causes a sliding relative motion of the liquid layers. In contrast, in extensional rheology, the stress is normal to the surface applying the stress. If the liquid is considered incompressible the volume is unchanged and we say this is an “isochoric” process.

The rheology of oscillating extensional stress differs substantially from traditional steady state extensional rheology. The isochoric condition might be violated when the extensional stress varies in time. Extensional nonisochoric rheology with oscillating extensional stress is called “longitudinal rheology.” There is an old review by Litovitz and Davis,<sup>18</sup> which presents in parallel both shear and longitudinal rheological theories.

Both shear and extensional stress cause displacement in the liquid. In the case of a step change in the shear stress, the liquid displacement propagates with a certain speed from the interface where it has been generated into the bulk. Eventually, it reaches some steady state condition within the entire system. Many modern rheometers, instead of applying a steady state stress, apply stress that varies in time. It is achieved by moving the interface backward and forward.

When the frequency of such oscillation is low, the displacement originated at the interface has enough time to fill the entire system during the first half of the cycle. All parts of the system would then experience displacement in one direction.

Increasing the frequency would eventually alter this situation. The direction of the interface motion would change before the displacement would fill the entire system. Consequently, there would be areas in the system with opposite displacements. Such oscillating stress creates a “wave” of displacement.

This is the point where rheology comes into contact with acoustics. Acoustics is a science that studies propagation of mechanical waves. There is a spatial characteristic of the waves called “wavelength.” It is a distance of wave propagation during a single period of oscillation. If the wavelength is much shorter than the size of the system, then the subjects of rheology and acoustics would merge.

This is situation that we consider in this paper. We will be dealing with waves of oscillating stresses, both shear and extensional. There are several different ways of generating these oscillations: rotating cylinders, shaking plates, vibrating surfaces of piezocrystals, etc., see Barnes,<sup>32</sup> Dukhin and Goetz,<sup>27</sup> Portman and Margraf,<sup>33</sup> Soucemarianadin *et al.*,<sup>34</sup> and Williams and Williams.<sup>35–37</sup>

There is a set of notions introduced in acoustics for characterizing these oscillating stresses. One of these notions is a frequency of oscillation, usually denoted as  $\omega$ . The other one is pressure  $P(x, t)$  at a given moment  $t$  and given point  $x$ . In the case of monochromatic oscillation at a single frequency, this pressure is usually expressed in terms of complex numbers,

$$P(x, t) = P_0 e^{-\alpha x} e^{j(\omega t - \omega x/V)}, \quad (\text{B1})$$

where  $P$  is pressure amplitude,  $\alpha$  is attenuation coefficient,  $V$  is a speed of stress wave propagation through the viscoelastic media, and  $j$  is  $\sqrt{-1}$ .

The attenuation coefficient determines how quickly the pressure amplitude decays with distance due to various dissipative effects. The units of the attenuation coefficient units are “nepers per meter” (Np/m). The unit “neper” is introduced because calculation of the attenuation coefficient requires taking the logarithm of the ratio of pressures at differ-

ent distances. There are different types of logarithms. The unit “neper” indicates natural logarithm. Alternatively, the unit “decibel” (dB) indicates decimal logarithm.

An alternative way to characterize the pressure decay is to use the notion of “penetration depth”  $x_0$ , where

$$x_0 = \frac{1}{\alpha}. \quad (\text{B2})$$

The pressure amplitude decays by a factor  $\ell$  from its initial value  $P_0$  when the distance traveled equals the “penetration depth,” where  $\ell \approx 2.71$ , the basis of the natural logarithm. The penetration depth differs from the wavelength  $\lambda$ , which depends mostly on frequency,

$$\lambda = \frac{2\pi V}{\omega} = \frac{V}{f}, \quad (\text{B3})$$

where  $f$  is frequency in *Hertz* (Hz).

The attenuation coefficient and the penetration depth are phenomenological and experimentally measurable parameters that are used in acoustics for characterizing dissipative processes. The speed of the wave propagation is related to the elastic properties of a liquid.

Rheology operates with a completely different set of notions for characterizing the viscoelastic properties of liquids. In the case of shear stress it is a “complex shear modulus”  $G^*$ , which has a real component “storage modulus”  $G'$  and an imaginary component “loss modulus”  $G''$ ,

$$G^* = G' + jG''. \quad (\text{B4})$$

In a manner similar to shear rheology, Litovitz and Davis<sup>18</sup> introduce a “complex longitudinal modulus”  $M^*$ , which corresponds to the longitudinal rheology case, where

$$M^* = M' + jM''. \quad (\text{B5})$$

However, it turns out that these two moduli are in fact identical if one makes a suitable change in subscript. Therefore we will use the same symbol  $G^*$  for both of them, with the subindex “shear” for shear stress, and subindex “long” for longitudinal stress. Similarly, we will use the same indices for both the attenuation coefficient and penetration depth for distinguishing between these two types of stress.

The above-mentioned similarity appears in the general relationship between acoustic and rheological parameters for both stresses. Functionally these relationships are the same for both stresses,

$$G'_{\text{shear}} = \rho \omega^2 V^2 \frac{\omega^2 - \alpha_{\text{shear}}^2 V^2}{\left[ \omega^2 + \alpha_{\text{shear}}^2 V^2 \right]^2} = \frac{\rho \omega^2 \left( \frac{4\pi^2}{\lambda^2} - \frac{1}{x_{0\text{shear}}^2} \right)}{\left( \frac{4\pi^2}{\lambda^2} + \frac{1}{x_{0\text{shear}}^2} \right)^2}, \quad (\text{B6})$$



$$G''_{\text{long}} = 2\rho\omega^3 V^2 \frac{\alpha_{\text{long}}^{\text{shear}}}{\left[\omega^2 + \frac{2}{\alpha_{\text{long}}^{\text{shear}}} V^2\right]^2} = \frac{\rho\omega^2 \frac{4\pi}{\lambda x_{0\text{shear}}}}{\left(\frac{4\pi^2}{\lambda^2} + \frac{1}{x_{0\text{shear}}^2}\right)^2}, \quad (\text{B7})$$

where  $\rho$  is the density.

It is possible to introduce shear viscosity and longitudinal viscosity for non-Newtonian liquids using the same expression for both parameters,

$$G = G' + iG'' = G' + i\omega\eta_{\text{long}}^{\text{shear}}(\omega).$$

The derivation of Eqs. (B6) and (B7) for the shear rheology case is from the paper of Williams and Williams,<sup>34–36</sup> who in turn make reference to a much earlier book by Whorlow.<sup>38</sup> The derivation of the identical equations for the longitudinal rheology case is taken from review by Litovitz and Davis.<sup>18</sup> They, in turn, make reference to much earlier works by Meixner,<sup>39,40</sup> who apparently derived general thermodynamic theory of stress-strain relationship in liquids.

Together, Eqs. (B6) and (B7) provide a general phenomenological link between acoustics and rheology. One can use them for calculating the shear loss modulus  $G''_{\text{shear}}$  and shear storage modulus  $G'_{\text{shear}}$  from the acoustically measured shear penetration depth  $x_{0\text{shear}}$  (or shear wave attenuation  $\alpha_{\text{shear}}$ ) and shear wave sound speed.

The same can be done for longitudinal parameters. The longitudinal loss modulus  $G''_{\text{long}}$  and longitudinal storage modulus  $G'_{\text{long}}$  is linked to the sound attenuation coefficient  $\alpha_{\text{long}}$ .

The whole difference between shear rheology and longitudinal rheology is comprised by the specific differences in the penetration depth. It is possible to make some estimates of the each penetration depth using well known theories.

The penetration depth of the shear stress  $x_{0\text{shear}}$  can be estimated using following well known equation for viscous boundary layer, see, for instance, Dukhin and Goetz.<sup>27</sup>

$$x_{0\text{shear}} \approx \sqrt{\frac{\eta}{\rho\omega}}, \quad (\text{B8})$$

where  $\eta$  is the dynamic viscosity.

Most liquids do not support shear waves very well, which means that the penetration depth is rather short. In water, for instance, the shear penetration depth is approximately 0.1 mm at a frequency of 100 Hz. It quickly decreases with frequency. In the case of ultrasound frequency of 1 MHz it is only about 10  $\mu\text{m}$  and becomes just 1  $\mu\text{m}$  at 100 MHz.

On the other hand, longitudinal waves are able to penetrate much further into the liquid. We can use Stokes's law, Eq. (9), for estimating the longitudinal penetration depth,  $x_{0\text{long}}$ . It yields the following simple expression for estimating  $x_{0\text{long}}$ :

$$x_{0\text{long}} \approx \frac{\rho V^3}{\omega^2 \eta}. \quad (\text{B9})$$

The longitudinal penetration depth is much longer than the shear penetration depth. In water, the longitudinal penetration depth is about 1000 m at 1 MHz, and even at 100 MHz it is 10 cm. Longitudinal waves propagate long distances in liquids. It is easy to generate and measure them.

One of the peculiarities of the longitudinal viscosity is the small value of the parameter  $(\alpha V/\omega)^2$ . As a result general equations for longitudinal viscoelastic modulus could be simplified and longitudinal viscosity equals

$$\eta_{\text{long}} = \frac{2\alpha_{\text{long}}\rho V^3}{\omega^2}. \quad (\text{B10})$$

The possibility of studying a much higher frequency range is a clear advantage of using longitudinal stress waves over shear stress waves.

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